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Inorganic Chemistry

PART I

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ORGANIC CHEMISTRY.

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PREFACE.

There is perhaps so little room for a new text-book on the elements of inorganic chemistry, and so little scope for any novel presentment of the subject, that it might well seem superfluous to add to the number of those already in existence, and impossible to do so except on well-worn lines.

But although most teachers seem to be fairly well agreed as to the ground to be covered in an ordinary three years' course, we believe that in one very important respect most of the present text-books leave something to be desired, and that is in the arrangement of the subject-matter, which, as a rule, does not correspond with all the requirements of the average student, with the lectures which he attends, or with his progress in the study of cognate subjects.

A boy commencing to learn chemistry at school has already a choice of many good text-books of a very elementary character suitable for his first year or matriculation course, but when he proceeds to a college or a university and begins his second year's or intermediate work, although he has again a wide choice, he must generally procure a different and much larger text-book and start again at the beginning; some of the new matter which he requires is scattered here and there in the earlier chapters dealing with the non-metals, most of it is contained in the chapters on the metals, but in both cases there is generally the further difficulty that it is not differentiated from the more advanced matter required in his third year. These are obvious disadvantages which we have attempted to remedy, and Part I. contains what we consider to be suitable and sufficient matter for the first year's course, of which Part II. will form a direct continuation.

In dealing with the subject-matter of Part I. we have been led to postpone the study of the atmosphere and of the common gaseous elements until the student has become familiar with chemical change in the case of other more tangible substances, such as copper and calcium carbonate; also to defer the consideration of the complex processes of ordinary combustion until the properties of carbon and those of some of its compounds have been described.

Rather more attention than is usual has been given to the determination of composition, which after all is one of the main objects of chemistry, but the description of the properties of elements and compounds has been restricted to what seemed necessary at this particular stage, and to what was possible without involving the use of other substances which had not been described.

Equations, which generally prove such a stumbling-block to beginners, have only been introduced after a description has been given of the properties of a number of compounds sufficiently large to serve as some basis for a presentment of the principal facts and theories on which molecular formulæ are founded; that an equation is an expression of experimental data is a fact which, we believe, is rarely realised by beginners in consequence of the premature use of symbolic notation.

The subject-matter of Part I. is essentially the same as that of the chemistry syllabus of the London University for the external matriculation examination, and that of the Board of Education for Stage I.

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'It is the object and chief business of chemistry to skilfully separate substances into their constituents, to discover their properties, and to compound them in different ways.

'How difficult it is, however, to carry out such operations with the greatest accuracy can only be unknown to one who either has never undertaken this occupation, or at least has not done so with sufficient attention' (Scheele, *Chemische Abhandlung von der Luft und dem Feuer*, 1777. Translated in the Alembic Club Reprint, No. 8).

INORGANIC CHEMISTRY.

PART I.

CHAPTER I.

Introduction.

MANY materials which are found on the earth are known by different names because they can be distinguished from one another. Gold, salt, water, oil, air, and coal-gas, for example, are easily distinguished from one another, because they have such very different effects on our senses.

When any material is examined, its effect on the sense of sight may be indicated by stating its size, shape, colour, and so on; its effect, if any, on the senses of smell, taste, and touch may also be expressed in words. Some of the qualities, attributes, or *properties* of the material are thus described.

But in addition to such external or outward qualities, many other properties may be discovered by examining the material in various other ways; thus, if a solid, the material may be tested as to whether it is brittle or malleable, dull or sonorous, rigid or plastic; it may also be heated to see whether it melts—that is to say, whether its properties change when its conditions are altered; it may also be mixed with some other material to see whether it is changed thereby, and so on.

Now when such methods of examination are used and the properties of a given material are considered, it is clear that some of these properties are much more distinctive than others. For example, if a sheet of the material called glass is broken into two pieces, and one is then ground to a fine powder, the two samples or specimens *differ* in certain properties; the single piece has a particular shape and size, and is smooth and transparent; the powder is made up of innumerable small '*particles*' of different shapes and sizes, and is gritty and not transparent as a whole; and yet it is known that the two samples are one and the same material, and if examined further they would be found to have most, if not all, remaining properties in common. Thus both would be tasteless and odourless; if heated sufficiently both would *melt*, and they would melt at the same temperature; if the melted samples, both of which are still the material glass, were cooled again, the two pieces so obtained might still differ in shape and size, but otherwise would be *identical* in properties, and both could be recognised as the material called 'glass.'

Hence it is necessary to make a distinction between those properties which are more or less accidental or variable, and those which really belong to, and are always shown by, a material; the shape and size are properties of the less important kind to which, as a rule, little attention need be paid; the other and more important properties, which are called **specific properties,** are those which serve to distinguish one material or substance* from another.

By studying the specific properties of the stuff or matter which forms the crust of the earth, the oceans and seas, the atmosphere, and animals and plants, many different materials or varieties of *matter* † may be recognised; the question then arises, why does one material differ from another? Why, for example, is gold different from salt? Are these two materials made of the same or of entirely different stuff or matter? What are they made of, or composed of? What is their *composition?*

---

* The sense in which the words 'material' and 'substance' are used is explained later (pp. 33, 34); *forward* references need not be looked up at a first reading.

† Anything which has *mass.* The terms 'mass' and 'weight' have not the same meanings, but the weight of any form of matter is directly proportional to its mass.

One of the principal objects of the science of chemistry is the study of the *composition of matter.*

But there are very few materials on the earth which do not change in one way or another. On a cold winter day water, which is a liquid, changes into a solid, ice; when the frost goes—that is to say, when the temperature rises—the ice passes again into the liquid, water. When water is heated sufficiently, it boils and changes into steam, the liquid passing into a *vapour;* when the vapour is cooled, it changes again into water.

Sugar and salt change when they are placed in water; the solids disappear. A bright piece of steel changes when it is left in the open air; it rusts and slowly becomes a reddish-brown powder. When paper, wood, or coal burns, it undergoes remarkable changes, and all that remains visible is a black or gray 'ash.' In living plants and animals changes of an even more remarkable kind take place; in plants, the air, water, and soil in which they grow are changed into 'vegetable matter;' in animals, vegetable matter, such as grass, corn, or other material taken as food, is changed into flesh, fat, and bone.

Another principal object of the science of chemistry is the study of the *changes* which matter undergoes, and of the conditions which bring about these changes.

In order to attain these objects the chemist makes trials, *tests*, or *experiments* with the matter which is being studied; he thinks of some suitable experiment to make, and then observes the results and states them as *facts;* from these facts he may draw inferences or conclusions, which are thus based on *experimental evidence.*

For instance, in the past many chemists have made experiments to try to find out what happens when an ordinary (dry) wax candle is burned in (dry) air, and they have observed that one result is, that steam or water is obtained; this is a *fact*. From this fact several inferences or assumptions or conclusions might be drawn. Thus it might be inferred or supposed that the water came from the candle alone, or that it came from the air alone, or that some of it came from the candle and some from the air; further experiments would then be made, until at last, perhaps, some definite conclusion could be drawn as to whence and why water is obtained under such conditions.

When from the results of experiments with all sorts of matter a great many separate facts have been established, it is often possible to express a large number of them in some general statement, which is then called a *rule*, a *generalisation*, or a *law;* thus the statement 'All vapours and gases change into liquids at sufficiently low temperatures' is a generalisation or law established by innumerable experiments.

A generalisation or law having been discovered, it is sometimes possible to go a step further and to speculate or make suggestions as to 'why' such a law holds good. Such speculations, which are termed *hypotheses*, are often of very great use, as they generally suggest and lead to further experiments, by means of which they may be 'tested' or put to the proof. If the hypothesis is not confirmed by the results of such experiments, if it no longer satisfies all the facts, then it is given up, and perhaps a new one is suggested; but if the additional results agree with it, and it is found to explain or fit in with a continually increasing number of facts relating to different occurrences or *phenomena*, the hypothesis becomes more valuable still, and may be called a *theory*.

It is by a series of steps from experiments to facts, hypotheses, and theories that the science of chemistry is advanced, and although such hypotheses and theories may prove useful only for a time and may then be displaced by new ones, the facts remain; the boundaries of knowledge have been permanently extended.

The knowledge thus gained is of the greatest service to mankind. The natural materials found on or in the earth can be so changed now by known 'chemical' processes that they become useful in all sorts of new and different ways. Thus, from earthy or stony masses of iron *ore*, a material which in a natural state is practically useless, the manufacturer prepares various qualities of steel; similarly, nearly all other metals, such as lead, copper, tin, and so on, are manufactured by chemical processes from natural ores, which otherwise would be valueless. It is difficult to imagine a world without these metals, or to realise what vast progress has been rendered possible by their manufacture; without them neither steam nor electricity could be utilised. In all great branches of industry chemistry plays an important part; in the manufacture of calico, linen, and other fabrics made of cotton, flax, wool, silk, and other fibres, chemical operations are necessary; the brilliant and many-hued dyes in use at the present day are nearly all prepared from coal-tar; glass, pottery, cement, soap, soda, and many other almost equally useful materials in daily use are manufactured in chemical-works; the explosives used for blasting and in warfare, illuminating agents such as coal-gas and acetylene, alcohol, chloroform, many paints, disinfectants, and medicines are all produced from natural materials by chemical operations. These examples may serve to indicate the great importance of the science of chemistry, and that the progress of civilisation is closely dependent on the application of chemical knowledge to the utilisation of the raw materials of the earth's crust.

As the science of chemistry is entirely based on experimental evidence, it is necessary that the student should understand the manner in which some of the principal facts have been established. For this purpose he should not only witness in the lecture-room as many experiments as possible, but he should also himself carry out a course of experimental work in the laboratory. During this work he should constantly bear in mind that the greatest care must be taken in order to establish a fact, and that in making experiments, even the simplest ones, it is necessary to observe the results very closely, not to confuse what *seems* to happen with what does happen, and to think of possible mistakes or sources of error. The more carefully the experiment is carried out, the more trustworthy is the evidence obtained from it and the more useful the training which the study of chemistry provides.

For the purpose of these experiments 'apparatus' is required. This consists principally of tubes and vessels, made of glass because of its transparency, and because it is seldom changed to any great extent by the materials under examination.

Since many materials which do not change at ordinary temperatures, or do so only very slowly, are rapidly altered at higher temperatures, a source of heat is required, and burning coal-gas is generally used. As the ordinary 'bat's-wing' or 'fish-tail' luminous flame deposits 'soot' on glass or other vessels, the flame obtained with a *Bunsen-burner* (fig. 1), so named after its inventor, is employed. In this burner the gas from the small tube (*a*) mixes with air which is drawn in through the openings (*b*) at the base of the larger tube (*c*), and the mixture is burnt at the top of (*c*). The flame has a high temperature, and does not smoke or deposit soot. The Bunsen-flame is also used in cooking-stoves and in the ordinary incandescent lamp (p. 134).

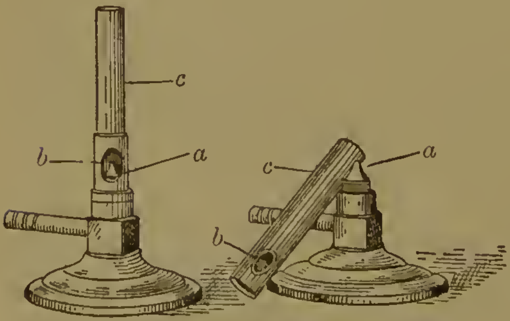

Fig. 1.

The flame of the *blowpipe-burner* (fig. 2) is used when a very high temperature is required; the principle of the burner is similar to that of the Bunsen, but a forced draught of air is obtained with the aid of a foot-bellows (placed on the floor). The movable metal part (*a*, *c*) consists of two concentric tubes; the outer one is connected with the gas-supply (*b*), and the inner one (*c*) with the bellows.

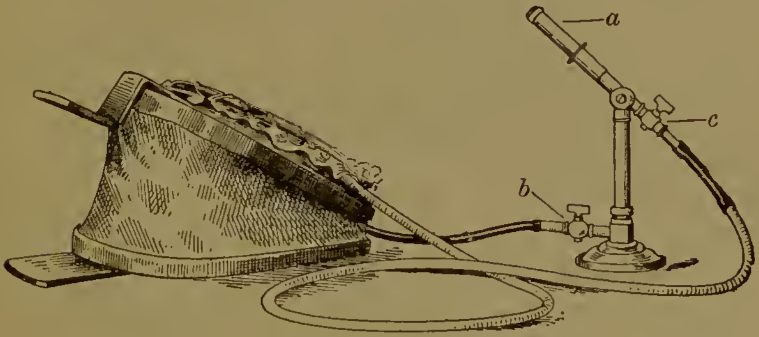

Fig. 2.

In heating a glass vessel it is advisable to do so gradually and to secure a uniform distribution of heat, otherwise the vessel may crack. For this purpose the vessel is generally placed on a piece of iron or copper gauze, on a sheet of asbestos, or on a layer of sand contained in an iron tray (sand-bath).

CHAPTER II.

Changes in State.

Melting.—When water is cooled to a certain temperature, which is called its freezing-point, the *liquid* changes into or becomes a *solid*, known as *ice*. This temperature is marked 0° on the Centigrade, 32° on the Fahrenheit scale, and is fixed by putting the thermometer into melting ice. From this statement it may be inferred that all samples of ice melt at the same temperature—otherwise two or more thermometers would not register the same freezing-point.

If any accurate Centigrade thermometer is placed in well-stirred melting ice (a mixture of ice and water), not only does the thermometer register 0°, but it continues to do so until *all* the ice is melted. Further, if some water is cooled in a vessel, which is surrounded by a freezing mixture of ice and salt,* until ice begins to form, a thermometer placed in the well-stirred freezing water again registers 0°, and continues to do so until *all* the water has solidified (frozen). Now, as this water, or ice, is not the same as that used in marking the freezing-point on the thermometer, it may be concluded that water freezes and ice melts at one and the same fixed temperature; this is called the *freezing* or *melting point* as the case may be.

Instead of using a freezing mixture, the water may be cooled by the evaporation of ether; a little ether is placed in a Woulff's bottle, fitted up as shown (fig. 3), and the water is contained in a test-tube, which passes through a band of india-rubber. On connecting the tube (a) to a water-pump, air is drawn through (b), the ether (c) evaporates rapidly, and its temperature is lowered sufficiently to freeze the water (d).

The tube (a) of the water-pump (fig. 4) is attached to a high-pressure water-tap; the water rushing through the nozzle (b) draws with it a stream of air and thus causes suction; the tube (c) is connected with the apparatus from which the air is to be pumped.

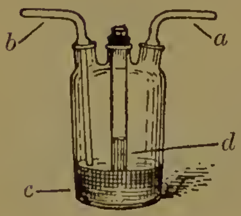

Fig. 3.

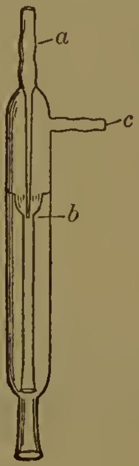

Fig. 4.

A substance which is solid at ordinary temperatures may now be studied in order to see whether it behaves in any way like ice. For this purpose some (pure) *naphthalene* (p. 125), a white solid which is deposited in gas-mains, is coarsely powdered and placed in a beaker, which is then heated on a water-bath (fig. 5);* after some time the naphthalene begins to melt; if it is then well stirred with a thermometer, it is found that the temperature at which naphthalene melts is 80°,† and that the thermometer remains at 80° until *all* the naphthalene is melted. When this is the case the liquid naphthalene is allowed to cool, stirring well with the thermometer; it is then found that the liquid freezes or solidifies again at 80°, and that the thermometer remains at this temperature until *all* the naphthalene has solidified. Every sample of (pure) naphthalene shows this behaviour, so that naphthalene, like water, has a definite freezing or melting point.

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* This mixture may give a temperature as low as −21° C.

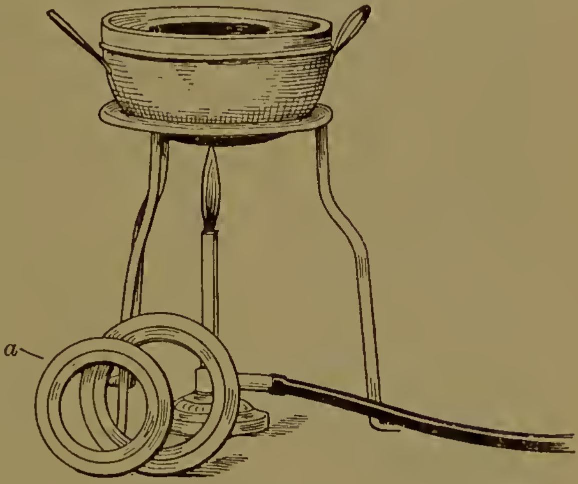

Fig. 5.

Similar experiments with other substances give similar results, which may be summarised as follows:

When a substance melts or freezes the change takes place at a fixed and definite temperature which is called the *melting* or *freezing point* (m.p.) of the substance (compare p. 19).

---

[*] The water or steam bath is used when a temperature not exceeding 100° is required; the cover is composed of broad concentric metal rings (*a*).

[†] All temperatures are expressed on the Centigrade scale.

Now if in the course of some experiments it were required to find out whether a given substance was or was not ice, its *melting-point* could be determined; if it melted at 0° this fact *alone* would not prove it to be ice, but if it melted at any other temperature, say 3° or 10°, it could not be ice.

The melting-point of a substance, therefore, is one of its important specific properties, and serves to distinguish it from other substances. It is obvious from this statement that although some of the properties of ice change when it passes into water, and *vice versâ*, yet the property of *changing* in a fixed manner under certain fixed conditions is itself a constant or specific property of this substance. The melting-points of some common substances are given later (p. 14).

If on a frosty day a bowl of rain-water and a bowl of salt-water are placed outside, equally exposed to the cold, the 'fresh'-water freezes, but unless there is a very hard frost the salt-water does not, if there is much salt in it; however, should the cold be intense enough to cause the salt-water to freeze, the ice on it melts before that on the fresh-water when the thaw sets in; salt-water, therefore, has a lower freezing or melting point than fresh-water. This is not in contradiction to the rule stated above, because salt-water is *not* water; it is water *and* salt, and may be called very *impure* water (p. 33).

Again, if some naphthalene (m.p. 80°) is mixed with about 10 per cent. of paraffin-wax, and the melting-point of this mixture is taken, it is found that the mixture *begins* to melt, say, at about 70°, but does not melt *completely* if kept at this temperature; when the temperature is slowly raised above 70° the mixture gradually becomes more liquid, but is not entirely melted until the thermometer indicates, say, 78°. Comparing this behaviour with that of (pure) naphthalene, and the behaviour of impure water with that of (pure) water, it is seen that when a substance is mixed with some other substance its melting or freezing point may be *lowered;* further, a part of the solid generally begins to melt several degrees lower than the remainder, so that the melting-point of the mixture is not definite, but ranges over several degrees.

As mixtures generally behave in this way, a determination of the melting-point of a solid often shows whether or not it is a mixture—a most useful and simple method. Tallow, paraffin-wax, butter, solder, glass, &c. examined in this way are found to be mixtures (p. 27).

Boiling.—When water is heated to a certain temperature which is called its *boiling-point*, the liquid changes into a *vapour* known as steam. This temperature is marked 100° on the Centigrade, 212° on the Fahrenheit scale, and is fixed on the scale by putting the thermometer in the vapour of boiling water. From this statement it may be inferred that all samples of water boil at the same temperature, and experiments confirm this conclusion (compare p. 18).

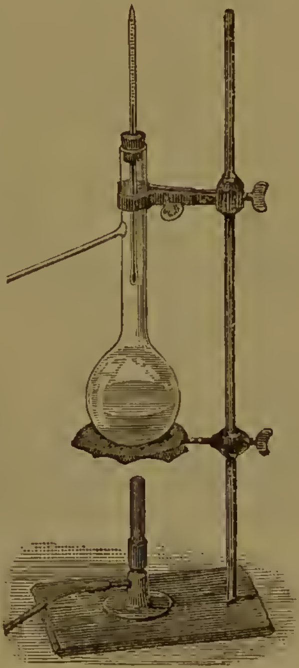

Fig. 6.

Some water is placed in a small distillation-flask (fig. 6)* fitted with a cork, through which there is passed a thermometer with its bulb some distance above the surface of the liquid; on heating with a Bunsen-flame, small bubbles form at the inner surface of the glass, rise in the water, and escape into the air. These bubbles are considered later (p. 96). As the water gets hotter, small bubbles are again produced at the bottom of the flask; these get larger and larger as they rise through the liquid, causing a rapid movement or circulation, and when the bubbles burst at the surface of the liquid the water is said to boil or to be in ebullition. As soon as this happens the thermometer, which before had risen only a few degrees, suddenly shoots up to 100°, and *remains* at this temperature as long as boiling continues. A mist or cloud is also seen escaping from the side-tube, although there is no visible mist inside the flask (steam is invisible), and a dry, cold object held in this mist is immediately covered with very small drops of *water* which form a 'dew.'

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* A few pieces of unglazed earthenware are also placed in the flask, as the water then boils more regularly, without 'bumping.'

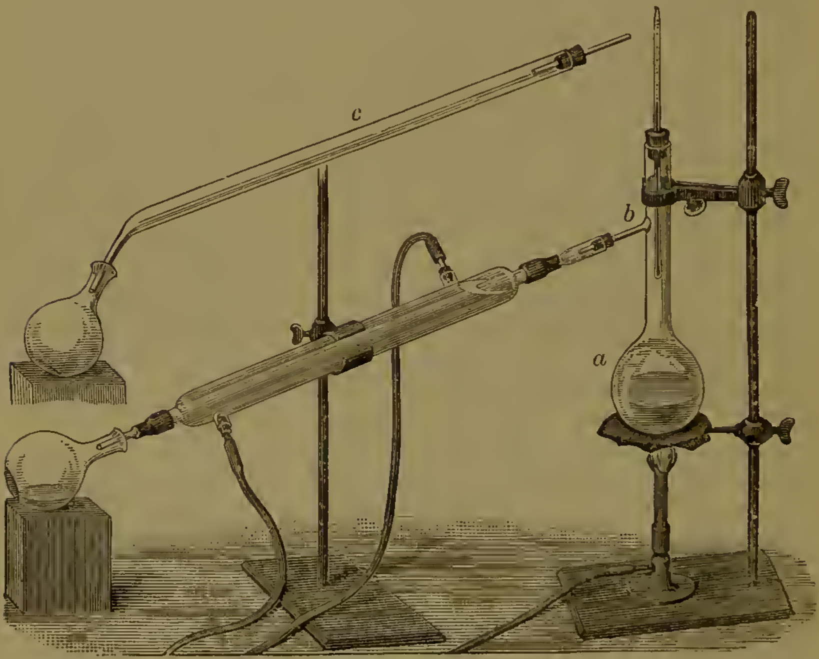

Fig. 7.

If a thermometer is held in the vapour just where the vapour is changing again into a liquid, the thermometer registers 100°.

Now as this water is not the same as that used in fixing the point marked 100°, it may be concluded that water boils and steam liquefies or *condenses* at one and the same temperature, which is called the boiling-point of the liquid (p. 18).

The liquid *benzene*, which is obtained from coal-tar, may now be studied, using a dry distillation-flask (*a*, fig. 7) and a thermometer as before. In this case, as benzene and its vapour are inflammable, the side-tube (*b*) of the flask is passed through a cork fitted into a *Liebig's condenser* (*c*).

This and other 'condensers' are used for rapidly cooling vapours; the vapour passes through the inner tube, which is kept cool by the flow of cold water through the outer jacket, and the liquefied or condensed vapour is collected in the *receiver*.

On heating the benzene, small bubbles do not appear at first, as in the case of water, but after a time large bubbles are produced, and finally the liquid begins to boil; the thermometer then shoots up to 80·5°, and remains at that temperature all the time that boiling continues; the benzene vapour, which, like water vapour, is invisible, is cooled in the condenser, and changes back to liquid benzene.

This process of boiling a substance, condensing the vapour, and collecting the liquid thus formed is known as **distillation**, and the portion which has been distilled is often called the *distillate*.

Any other sample of benzene boils at 80·5°; benzene, like water, has a definite boiling-point. Other liquids, such as ether and chloroform, when examined in a similar manner, give similar results, which may be summarised as follows:

When a liquid boils or a vapour liquefies, the change takes place at a fixed and definite temperature which is called the *boiling* (or *liquefying*) *point* (b.p.) of the substance.*

The melting and boiling points of some common substances are given on p. 14; † it will be seen that there is no apparent connection between them.

---

* This statement is only true when the *conditions* are fixed, as explained later (p. 18).

† All temperatures are expressed in the Centigrade scale. In taking temperatures higher or lower than those which can be indicated with a mercury thermometer, various other instruments are used.

	Melting-Point.	Boiling-Point.		Melting-Point.	Boiling-Point.
Chloroform	–70°	61°	Mercury	–39·4°	360°
Benzene	6°	80·5°	Sulphur	114·5°	448·4°
Water	0°	100°	Zinc	412°	920°

Now if a liquid were being examined and it was required to find out whether or not it was benzene, its boiling-point could be determined in the manner described above; if this was 80·5° it would be possible that the liquid might be benzene, whereas if the boiling-point was 70° or 90° the liquid could not be benzene.

The boiling-point of a substance (which may be either solid or liquid at ordinary temperatures) is one of its important specific properties which may serve to distinguish it; if in addition to the boiling-point the melting-point is found to be that of a particular substance, the evidence becomes almost conclusive. Thus, if a substance melts at 0° and boils at 100° it is almost certainly water; if it melts at 6° and boils at 80·5° it is almost certainly benzene.

When by such means, or in other ways, the nature of a substance is conclusively established, the substance is said to have been *identified.*

The melting-point and boiling-point of a substance are called *physical constants* of that substance; the density or specific gravity * is another specific property and physical constant often used for the identification of a substance.

If instead of benzene some methylated spirit is heated in the distillation apparatus (fig. 7), it behaves quite differently from water or from benzene; although the thermometer shoots up to about 80° when the spirit begins to boil, it does *not* remain at that temperature, but rises slowly during *distillation* and finally registers 100°. This is because methylated spirit is not a *pure* liquid but a mixture (p. 32); since such mixtures nearly always have an indefinite or gradually rising boiling-point, a distillation of the *whole* of any liquid (where possible) may show whether it is or is not a mixture. This is a very important and simple method of examining liquids (p. 32). Spirits (brandy, whisky, gin), paraffin-oil, turpentine, coal-tar, &c. examined in this way are found to be mixtures.

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* The density or specific gravity (sp. gr.) of a solid or liquid is the weight in grams of one cubic centimetre of the substance at 4°; the density or sp. gr. of water at 4° is 1.

Although ice, water, and steam are very different in some respects, they all consist of one and the same kind of matter, which can be recognised or identified by its specific properties. When water freezes, nothing having weight is added to or taken from it; it merely becomes solid water. Similarly, when water is changed into steam, it merely becomes water in the form of vapour.

The changes which occur when a solid melts, a liquid solidifies, a liquid boils, or a vapour or gas liquefies are called **changes in state**; it is obvious that changes in state are *reversible*, and that the direction in which the change occurs depends on the *conditions* under which the substance is placed (compare p. 19).

Evaporation.—A little water placed in a saucer disappears in a day or two; although the water is far below its boiling-point, it passes into a vapour which mixes with the air, and the water is said to *evaporate* or to *vaporise.*

A little spirit poured on to a slate evaporates in a few minutes, although far below its boiling-point; a little ether evaporates much more quickly.

So that whereas the change, liquid ⟷ solid,[*] takes place at a fixed temperature, this is not so as regards the change, liquid ⟷ vapour; liquids, and even many solids (ice,[†] naphthalene), pass into vapour at temperatures far below their boiling-points. As the temperature rises evaporation takes place more and more quickly, and finally the liquid begins to boil.

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[*] The sign ⟷ indicates a change which is *reversible.*

[†] If after a light fall of snow the weather remains clear and frosty, the snow may disappear in a day or two owing to its evaporation.

Atmospheric Pressure. — The 'pressure of the atmosphere' or 'atmospheric pressure' is generally recorded in the newspaper weather reports, and is expressed in inches. To demonstrate the meaning of this expression and the nature of a *barometer*, which is the instrument used to measure the pressure, the following experiment may be made:

A stout glass tube (*a*) about 32 inches in length is sealed at one end; to the open end a piece of glass tubing (*b*) about 10 inches long is fastened by means of stout india-rubber tubing, and fixed vertically in a clamp (fig. 8); the whole tube is then filled with mercury to within about 6 inches of the top of (*b*) while in the slanting position shown in the diagram. The tube (*a*) is next gradually raised and fixed as shown in fig. 9. The mercury falls in the tube (*a*), and after oscillating for a short time comes to rest in some such position as that shown.

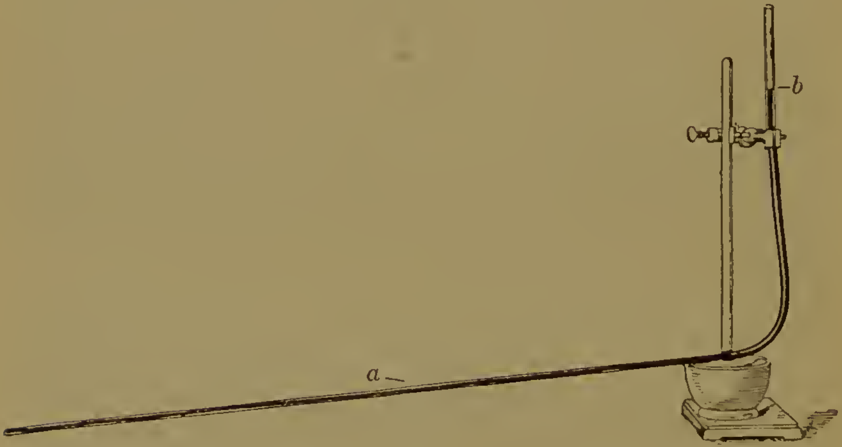

Fig. 8.

The experiment may also be made with a straight tube about 32 inches in length and closed at one end; this tube (*c*, fig. 10) is filled with mercury, closed with the thumb, and then inverted in a trough of mercury.

The columns of mercury in the tubes (*a*) and (*c*)* are held up by the pressure of the air; although the air is a gas it has weight, and the weight of the air pressing on the surface of the mercury in the tube (*b*) balances the mercury column (*xy*), that is to say, the column of mercury in the tube (*a*) above the level of the mercury in (*b*). Similarly

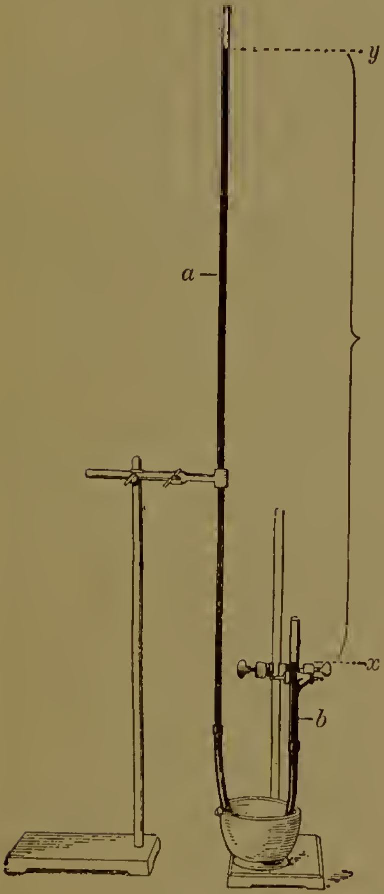

Fig. 9.

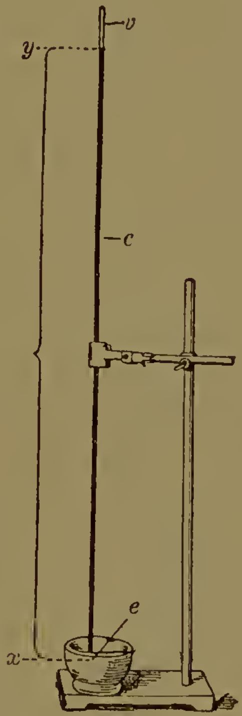

Fig. 10.

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* The empty space (*v*) above the surface of the mercury in (*a*) and in (*c*) is known as the Torricellian vacuum, so named after Torricelli, a pupil of Galileo, the discoverer of the atmospheric pressure.

the pressure on the mercury in the trough (*e*) supports the column (*xy*) in the tube (*c*). The weight or pressure of this column of mercury is equal to the pressure of the atmosphere; the instrument used to measure it is called a *barometer*—hence the term barometric pressure.

At sea-level the *average* pressure is equal to that of a column of mercury 760 millimeters (29·92 inches) in height;* this standard pressure, called one *atmosphere*, is equal to about 14·7 pounds per square inch of surface.

Relation between Boiling-Point and Pressure.—When water is boiled some way up a mountain its boiling-point is below 100°; at the top of the mountain its boiling-point is lower still, and the higher the mountain the lower the boiling-point.† Similarly with benzene and other liquids.

The boiling-point of a liquid, therefore, depends on the *pressure:* the lower the pressure the lower the boiling-point. This may be easily shown experimentally. A distillation apparatus like that shown in fig. 7 is arranged, but the lower end of the condenser is passed through a cork fitting tightly into the neck of a second distillation-flask; the side-tube of the latter is connected to a water-pump (p. 8) by means of stout india-rubber tubing. The water is then heated and the pump is started, whereupon some of the air is sucked out of the flask and the pressure is reduced; the water then boils at a temperature below 100°, and the more the apparatus is 'exhausted' the lower the boiling-point. Other liquids examined in a similar manner are found to boil or distil at temperatures below their *ordinary* boiling-points.

The process just described is termed *distillation under reduced pressure.*

The boiling-point may be now defined as that temperature at which the pressure of the vapour of a substance is equal to the pressure upon it. There is thus a definite and fixed boiling-point for every pressure.

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* On the top of a mountain the pressure is less, as there is a shorter column of air above. By observing the height of the barometer on the top of a mountain the altitude of the mountain may be ascertained.

† It is thus possible to find the height of a mountain by determining the boiling-point of water at the summit.

The boiling-point of water under different pressures is given in the following table, and it will be seen that the boiling-point varies greatly with a change in pressure. A diminution of pressure of 234·5 mm. causes the b.p. to drop from 100° to 90° (whereas an increase of pressure from 1 to 15·5 atmospheres raises the b.p. from 100° to 200°). Since the boiling-point of a liquid rises as the pressure is increased, when a vapour is subjected to an increase of pressure some of the vapour may be condensed although the temperature is not lowered; thus steam at 100° and 760 mm. pressure is condensed to water when the pressure is increased.

Pressure in mm.	Boiling-Point.	Pressure in mm.	Boiling-Point.
23·5	25°	525·5	90°
54·9	40°	733·2	99°
92·0	50°	760	100°
178·9	64°	787·7	101°

In the case of the melting-point, the variation with change of pressure is very small and may be neglected.

Sublimation.—When naphthalene, iodine, or sal-ammoniac is gently heated, say in a large flask, the substance may change directly into the state of vapour, without first melting, and when the vapour reaches the colder portions of the vessel it changes to the solid state, without first liquefying; substances which show this behaviour are said to *sublime* or to give a *sublimate*, and the process is termed *sublimation.*

The principal facts concerning such changes as those considered may now be summarised: Many varieties of matter may occur in one of three states—solid, liquid, vapour or gas.* All vapours and gases may be liquefied and all liquids may be frozen,† but some solids cannot be melted and some liquids cannot be boiled (p. 114).

Which of these states will exist (if more than one is possible) depends upon (*a*) temperature, (*b*) pressure. At one particular temperature and at one particular pressure all three may exist together; ice, water, and water vapour, for example, exist together at 4·6 mm. pressure and 0·007° C. At any other temperature than that at which the three states of one substance may exist simultaneously, or at any other pressure, one, or two, of the states disappear. Changes in state, therefore, are **reversible.**

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* The difference between the terms 'gas' and 'vapour' is explained later (p. 163).

† Only one known liquid has not yet been solidified.

CHAPTER III.

Solution and Determination of Solubility.

Solution of Solids.—When sugar is placed in water the solid gradually disappears; it has *not* melted, but has *dissolved*, and the liquid is called a *solution* of sugar in water, or an aqueous solution of sugar. Many substances dissolve in water, as, for example, salt, sugar, washing-soda (p. 35), blue vitriol (p. 36), nitre (p. 35); such substances are said to be *soluble* in water, and the water is called the *solvent.*

When water in which sugar has been dissolved is vigorously stirred, and a few drops of the solution are taken from *any part* and tasted, the presence of sugar in that part is recognised. Similarly with a solution of salt; whereas with blue vitriol, the presence of the dissolved solid in every part of the liquid is shown by the colour.

Now if some finely powdered blue vitriol, salt, nitre, or other soluble substance is added to a limited quantity, say 50 c.c., of cold water, a little at a time, and the liquid is stirred well, the blue vitriol (or other soluble substance) dissolves, quickly at first, then more slowly, and finally not at all, the last portion added remaining in the solid state at the bottom of the vessel. The solution cannot dissolve any more of the solid, and is said to be *saturated;* a solution which can still dissolve more of the solid is called *unsaturated.*

When the cold saturated aqueous solution of blue vitriol is gently warmed, the solid at the bottom dissolves. By raising its temperature, the solution is become unsaturated and takes up a further quantity of the solid; in other words, hot water dissolves a greater weight of blue vitriol than does cold water; but on adding more blue vitriol still, the hot solution also becomes saturated. When the hot saturated solution is cooled, the cold water cannot hold all the blue vitriol in solution, and some blue vitriol separates in the solid state.

The behaviour here described of water and blue vitriol is the ordinary behaviour of a solvent towards a soluble *solid* substance; in a few cases the solvent dissolves a greater weight of a given solid at low than at higher temperatures, but in all cases the weight of a given solid dissolved by a fixed weight of a given liquid at any fixed temperature is *constant*.

The weight of a substance does not change when it passes into solution. If some blue vitriol and water are placed on one pan of a balance in separate vessels and counterpoised, no change in weight is observed when the solid is dissolved in the liquid.

Concentration.—When a *dilute* aqueous solution of blue vitriol—that is to say, a solution which is far from saturated—is heated in the distillation apparatus (fig. 7), the water boils and the liquid which distils into the receiver is colourless and does not contain any blue vitriol; should the solution contain salt, sugar, or other solids as well as blue vitriol, these would all remain in the distilling-flask. The *solvent* can thus be separated from the dissolved substances by *distillation* (p. 13), and when the distillate is water it is called *distilled water;* ordinary water contains in solution substances which it has dissolved from the soil, &c., and from which it is easily separated by distillation.

Some of the solvent having been distilled away, the originally dilute solution is said to have become more *concentrated* *

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* When water has been added to a solution the latter is said to have been *diluted* with water.

—that is, it now contains a larger proportion of the dissolved substance in a given volume, and, though hot, may be saturated; in this case it deposits some of the solid when it is cooled. So that no matter how dilute the solution may be to start with, the dissolved substance may (as a rule) be recovered in the solid state by concentrating sufficiently. For this purpose an aqueous solution is generally heated in an open (evaporating) basin on a water-bath (fig. 5), and if the process is continued until *all* the solvent has vaporised the solution is said to have been *evaporated to dryness.* A liquid or solid which distils or vaporises is said to be *volatile;* one which does not vaporise is said to be *non-volatile.* Few common solids are so volatile that they distil over with water vapour.

Filtration.—When powdered chalk is placed in cold water it does not dissolve; it is *insoluble* in water, and the solid particles remain *in suspension* or sink. Many other solids are insoluble in water, as, for example, copper, charcoal, sulphur, and naphthalene. A solid which is insoluble in one liquid may be soluble in another; thus sulphur is soluble in carbon disulphide (p. 216), and naphthalene is soluble in alcohol (p. 126).

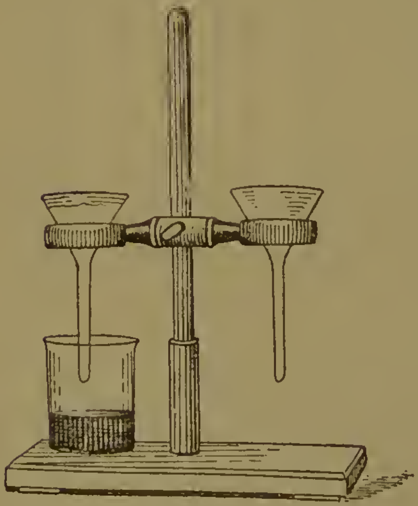
Fig. 11.

A solid in suspension may be separated from the liquid not only by distilling off the liquid, but also by the process of *filtration.* When, for example, water containing chalk in suspension is poured into a funnel (fig. 11) fitted with a cone of unglazed paper (blotting or filter paper), the water passes through the minute pores of the paper, but the particles of chalk do not; the filtered liquid or *filtrate* is quite clear; muddy or dirty water is filtered through beds of gravel and sand.

The term insoluble is not used very strictly, and in fact there are few solids which do not dissolve in an unlimited quantity of water. Thus chalk, which is generally called insoluble, dissolves in about 100,000 times its own weight of water. The term insoluble means, therefore, that the proportion of solid in the saturated solution is so small that for practical purposes it may be neglected. When a solid is only 'sparingly' soluble it is not easy to tell whether it is really soluble or not by merely placing it in the liquid; in such cases, after shaking the solid with the solvent for some time, the liquid is filtered and the filtrate is evaporated to dryness. If there is an appreciable *residue* (best observed by evaporating in a glass vessel) the solid is soluble; if not, it is insoluble.

Determination of Solubility.—The weight of a solid which is contained in a given weight of any saturated solution at a given temperature may be determined; by simple calculation, the weight of the solid dissolved by 100 grams of the solvent may then be found. The figures thus obtained represent the *solubility* of the given substance in the given solvent at the given temperature. In order to determine the solubility of salt, for example, the solid is added, a little at a time, to about 20 c.c. of distilled water, until some remains undissolved even after stirring the solution well for ten minutes; after noting its temperature, the solution is filtered (so that all undissolved salt is removed) into a *weighed* basin; the basin and the filtrate are then weighed together, and the solution is evaporated to dryness on a water-bath; the basin and the residue are then weighed until constant.*

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* As it is impossible to tell by the appearance of the residue whether all the water has been driven off or not, the basin and contents, which have been weighed once, are *again* heated at 100°, allowed to cool, and weighed

Example.—Temperature of saturated solution, 15° C.

Weight of basin = 20·4 grams. Weight of basin and solution = 30·6 grams. Weight of basin and residue = 23·1 grams.

Hence 10·2 grams of solution consisted of 7·5 grams of water and 2·7 grams of salt.

The *solubility* of salt in water at 15°, therefore, is 36, this being the weight of salt in grams dissolved by 100 grams of water.

An experiment such as this, in which weight is considered, is called a *quantitative* experiment; one in which only nature, character, or quality is considered is called a *qualitative* experiment.

In all quantitative experiments, even in such simple ones as determinations of solubility, it is difficult to obtain accurate results, and when any such experiment is repeated several times by the same or by different persons the results are not *exactly* the same; this is because there are certain causes or sources of error, more or less difficult to avoid, which affect the result, and which are summed up in the term '*experimental error.*' The greater the care taken—that is, the more the experimental error is lessened—the more nearly do the separate results agree with one another. As in most cases it is probable that some of the results will be too great (high), others too small (low), the *average* result may be taken as the most correct value.

The accuracy of the results depends, of course, to a great extent on the accuracy and sensitiveness of the scales or *balance* which is used. The delicate instrument required for accurate work should be carefully studied and treated with great care.

As the solubility varies with the temperature, but has a definite numerical value for every temperature at which a solution can be obtained, when these values have been determined experimentally for a sufficiently large number of different temperatures, the results may be expressed by a curve, the *solubility curve;* this curve then shows the solubility at *all* temperatures between the limits examined.

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again; only when the weight becomes constant—that is to say, when two successive weighings give the same result—is it known that all the water has been expelled. This process of *weighing until constant* has to be carried out in nearly every quantitative experiment.

Thus in the case of nitre (potassium nitrate) experiments give the following results, some of which are expressed by the solubility curve (fig. 12):

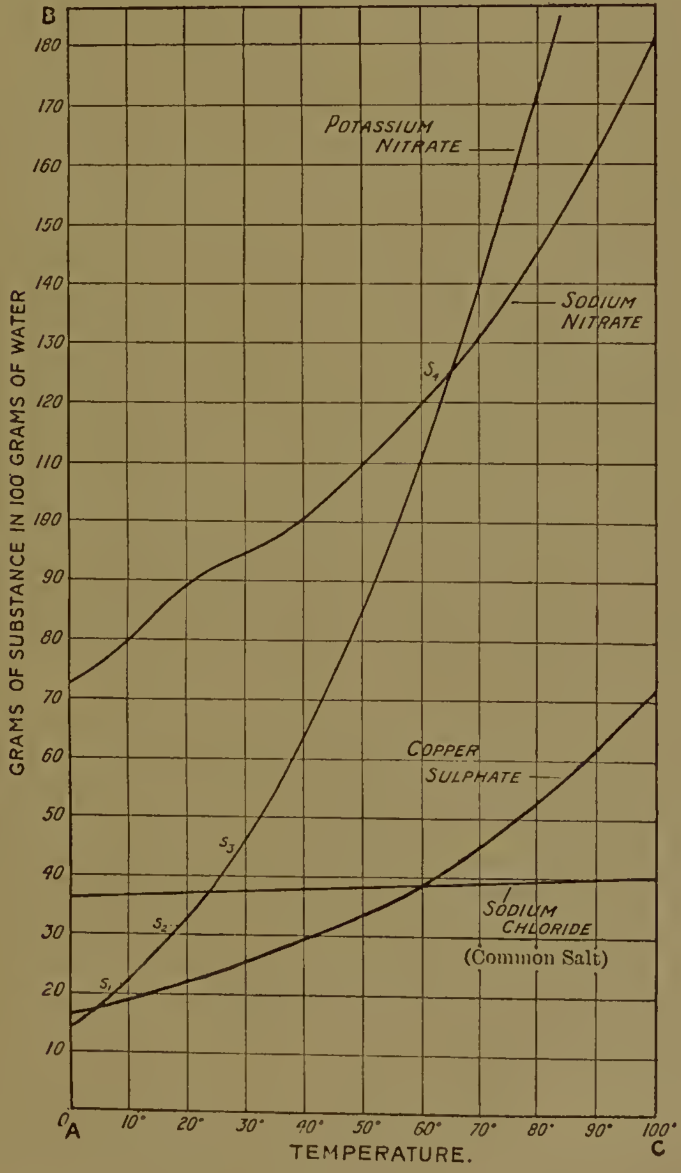

Fig. 12.

Temperature.	Grams of Nitre in 100 g. of Water.	Temperature.	Grams of Nitre in 100 g. of Water.
0°	13·0	60°	111
10°	21·1	70°	139
20°	31·2	80°	172
30°	44·5	90°	206
40°	64·0	100°	247
50°	86		

In order to draw the solubility curve the vertical and horizontal lines AB, AC are marked off from A in equal divisions, those on one line, say AB, representing grams of nitre dissolved by 100 g. of water, those on the other line, AC, the temperature at which the solubility is determined; a vertical line is then drawn from the point 10° on AC, and a horizontal line from the point 21·1 on the line AB; these meet at S_1. Taking the results for other temperatures, points S_2, S_3, &c. are obtained in a similar manner; finally these are joined by a curve, as shown in the diagram.

If now the solubility of nitre is required at any temperature between 0° and 100°, say at 65°, this can be found by drawing a vertical line from 65° on AC until it meets the curve at S_4, and a horizontal line from S_4 until it meets AB at a point which then gives the required value.

The solubility curves for a few other substances are also given in the diagram.

Solution of Liquids.—When spirit of wine (alcohol) is poured into water it immediately dissolves; a similar result occurs when water is poured into alcohol. These liquids dissolve one another, and either may be regarded as the solvent. The solubility of one in the other has no limit. Such liquids which can be mixed in all proportions are said to be *miscible* with one another. Turpentine, ordinary oils, petrol, and many other liquids are not miscible with water, and are, in fact, *insoluble.* Some liquids, such as ether, are soluble in, but not miscible with, water.

Solution of Gases.—The effervescence of soda-water, beer, &c. is due to the escape of gas from its solution in the liquid. The study of solutions of gases may be deferred (p. 163).

The solubility in a given solvent is an important specific property and physical constant of a substance, and serves for its *identification;* thus, if the solubility of a given solid is found to be 35·8 at 10°, it is possibly common salt; if in addition its solubility at 50° is 36·9 (see diagram, p. 25), then it is almost certainly salt, as it is extremely improbable that any other substance would have exactly the same solubilities as salt at these two different temperatures.

CHAPTER IV.

Mixtures and Substances.

When ground salt and sifted sugar are stirred or shaken together there results a *mixture,* something containing (at least) two distinct substances, which are called *components* (laid together) of the mixture. If after being stirred for a few seconds two samples of the mixture were taken from different parts, they would probably not be the same; they would differ (principally) in *composition,* as they would not contain the same proportion of salt (or of sugar.) Such a mixture, any part of which differs from any other in composition, is called a *heterogeneous* mixture.

If now this heterogeneous mixture is placed in a mortar and the components are ground together for, say, ten minutes, then two small portions or samples taken from different parts would not differ in composition so much as before, and might be almost identical; an *intimate* mixture of salt and sugar would have been obtained. Finally, after prolonged grinding, the mixture would be so intimate that samples taken from any parts of it would have the same composition—that is to say, all the samples would contain the *same* proportion of salt (and of sugar); in this respect, therefore, the mixture *might* now be called *homogeneous.*

But as the change from heterogeneous to homogeneous takes place gradually, it is impossible to say when the mixture would first *seem* to be homogeneous; really this depends on the *weights* of the samples taken and on the accuracy or delicacy of the methods of examination. Even after being stirred for a few minutes only, if the whole mixture were divided into two roughly equal parts the samples would probably have almost the same composition; whereas even after grinding for a year, if two samples, each consisting of three microscopic grains only, could be taken, one of these might contain two grains of sugar to one of salt, the other two of salt to one of sugar. Further, if various samples were examined with the naked eye all the mixtures might look homogeneous, whereas under a microscope they might appear heterogeneous; that is to say, particles of sugar and of salt might be recognised.

So the terms homogeneous and heterogeneous when applied to mixtures of *solids* are only *relative*. A mixture of solids which by itself might be considered homogeneous, would be heterogeneous in comparison with a solution of a solid, or that of a liquid; in solutions the particles of the dissolved solid or liquid and those of the solvent are so minute and so intimately mixed that it is difficult to imagine two samples, however small, being different in composition. This is also true in the case of a mixture of gases.

Now most of the ordinary materials of which the earth's crust is composed are mixtures, more or less heterogeneous. Some rocks, such as granite, some samples of sand, soil, coal, most vegetable and animal matter, are obviously heterogeneous; clay, slate, and many other materials which to the naked eye may *seem* to be homogeneous are, in reality, mixtures. Salt, on the other hand, and sugar are not mixtures and *are* homogeneous; the smallest conceivable sample of (pure) sugar contains sugar and nothing else.

Sometimes the words homogeneous and heterogeneous are used in reference to the similarity or difference in *size* and *shape* of the particles or pieces of a solid; in chemistry the mechanical condition of a solid substance is seldom considered (compare p. 2); a sample composed of 'loaf,' 'crystallised,' and 'sifted' sugar would be regarded as chemically homogeneous so long as it consisted of sugar and nothing else.

METHODS OF SEPARATING THE COMPONENTS OF A MIXTURE.

Mechanical Processes.—The separation of the components of a mixture is an operation which has to be carried out very often, and there are many different ways of doing so. Some of the simpler methods may be first considered.

Some 'crystallised' sugar is merely shaken with coarsely powdered blue vitriol; in such a mixture the crystals of the sugar can be picked out. If the mixture were ground to a fine powder the two components would still be there, but they could not be separated in this simple manner.

Some iron filings are shaken with some sand; the heterogeneous mixture is spread on a piece of paper and a magnet drawn over it; the iron filings only are attracted, and the heterogeneous mixture is separated into its components. If the particles of iron differ in size from those of the sand, the separation might also be accomplished by using a sieve of suitable fineness.

Some ground charcoal is mixed with some iron filings, the heterogeneous mixture is thrown into a deep vessel, and a rapid stream of water is sent through a pipe reaching nearly to the bottom of the vessel; the lighter charcoal is carried away, and the iron filings remain.

These are simple examples of what may be called rough *mechanical* processes, and such as a rule give only poor results—that is to say, the separation is not complete; for this reason they are little used in chemistry except in a few manufacturing operations.

Methods of Separation based on Solution.—Some salt and some chalk are mixed together, and the mixture is placed in water. The salt is soluble, the chalk is not. The solution is filtered (p. 22). Most of the salt is now in the filtrate, and the chalk is on the filter-paper. In order to obtain a complete separation, a little distilled water is blown on to the chalk from a wash-bottle (fig. 13); * this washes away some of the salt solution still remaining in the chalk and in the pores of the paper. On continuing this *washing* the whole of the salt is obtained in the filtrate, and can be recovered by evaporating the solution to dryness (p. 22). The salt and the chalk have now been separated.

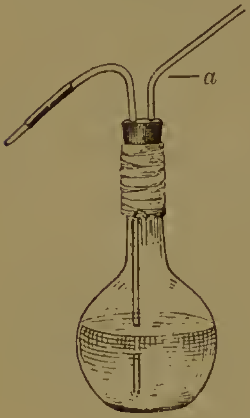

Fig. 13.

Ordinary gunpowder is a heterogeneous mixture of sulphur, nitre, and charcoal. Some gunpowder is shaken with carbon disulphide (p. 216), in which sulphur is readily soluble, the other two components being insoluble; the solution is filtered and the residue washed with carbon disulphide until free from sulphur; the filtrate is then evaporated † to obtain the sulphur. The mixture of nitre and charcoal, which remains on the filter, is transferred to a beaker, and when most of the carbon disulphide left in it has evaporated, some hot water is added; only the nitre dissolves, and after filtering the solution and washing the residue the filtrate is evaporated. The charcoal remains on the filter. The three components of the mixture are thus separated.

Such a method, based on a very great difference in their solubilities, is of the greatest importance in separating the components of mixtures.

Crystallisation.—When a hot saturated solution of a solid

* On blowing into the tube (*a*) a fine jet of water is expelled from the nozzle. The neck of the flask is wrapped round with felt so that the apparatus can be handled even when the water is nearly boiling.

† Carbon disulphide has an unpleasant smell, and is highly inflammable; the solution is evaporated in the apparatus shown in fig. 7, the flask being heated on a *water-bath*, or it is allowed to evaporate *spontaneously* (without being heated) in the open air.

(blue vitriol, nitre, sulphur) in any solvent is allowed to cool, or concentrated, some of the solid is thrown out or deposited. The particles of the solid thus produced are generally bounded by *plane*, reflecting, *surfaces* (faces) which meet, forming solid angles; they have a definite *geometrical* form, and are spoken of as *crystals*. A solid which is composed of crystals is said to be *crystalline*, and is thus distinguished from an *amorphous* solid, such as charcoal, which has no definite geometrical form.*

All the crystals of a given solid have the *same* geometrical form, although they may be of different sizes; thus crystals of common salt are all cubes, those of alum are regular octahedra. The *crystalline form* of a substance is a very important specific property and *physical constant*, which serves for the identification of that substance.

Crystals produced *rapidly* are generally small and *imperfect*—the geometrical form is incomplete; when grown *slowly*, by cooling a solution very gradually, or by allowing the solvent to evaporate at ordinary temperatures (spontaneous evaporation), they are larger and may be *perfect* in form. The small crystals of which a lump of loaf-sugar is composed and the large crystals of 'crystallised sugar' or sugar-candy afford an example of this difference; also those of an ordinary lump of sulphur compared with those obtained by the spontaneous evaporation of a solution of sulphur in carbon disulphide.

Crystals are generally formed when a liquid *solidifies*, as in the case of water, and melted naphthalene or sulphur; also when a vapour condenses directly to a solid—that is to say, in the process of sublimation (p. 19). An operation which leads to the formation of crystals, or the change from the liquid to the crystalline state, is termed *crystallisation*.

The process of crystallisation (from a solvent) is of the greatest use in separating the components of mixtures. If a powder composed, say, of 90 per cent. of blue vitriol and 10 per cent. of sugar is dissolved in the least possible quantity of boiling water and the solution then allowed to cool, *some* of the blue vitriol is deposited in crystals, because the cold solution is more than saturated with it; the cold liquid, however, is *not* saturated with sugar, *all* of which remains in the solution, which is now called the *mother liquor*. The crystals of blue vitriol may be separated by filtration, but some of the mother liquor, which contains sugar, is retained by them; if now they are *washed* (p. 30) with a very little cold water, all, or nearly all, the sugary liquid is removed. The crystals may then be redissolved in the least possible quantity of boiling water, and obtained again by cooling the solution; the solid has now been *recrystallised*, and may be separated by filtration from the mother liquor and dried in the air. A small proportion of the blue vitriol is thus obtained free from sugar.

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* Very few (pure) solids are known which cannot be obtained in crystals; most amorphous materials, such as glass, glue, gelatine, shellac, &c., are mixtures.

This process of separating the components of a mixture by the use of a solvent in which a part or the whole of the mixture dissolves is termed *fractional crystallisation.*

*As a rule it is difficult to obtain both or all the components of a mixture free from the others by fractional crystallisation, because finally the mother liquors become saturated with more than one component, and the *deposits* are then mixtures. It may also be noted that it is not necessarily the component of lowest solubility which separates first, but that with which, owing to the quantity and solubility combined, the solution is saturated.

Fractional Distillation.—Alcohol, which burns, and water, which does not, are *miscible* (p. 26); by adding sufficient water to some alcohol there results a mixture which does not take fire when a light is put to it. If now this mixture is heated in a distillation apparatus (fig. 7), the thermometer, which suddenly shoots up to about 80° or 85° when the liquid begins to boil, does *not remain constant*, but gradually rises during distillation until finally it reaches 100°. If the first portion or fraction of the distillate, say the first 5 per cent., is collected separately, this liquid burns when a light is applied to it; it contains a much larger proportion of alcohol than does the original mixture, because alcohol has a lower boiling-point (78°) than water (100°). This method of separating mixed liquids is termed *fractional distillation.*

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* The study of those parts of the text marked in this way may be postponed until the student commences the intermediate course.

Using one or other of the methods described above, or a combination of them, it is sometimes possible to separate one or more of the components of a mixture from the others; the component is then said to have been *isolated.* If it is quite free from every other component it is said to be *pure*, and is spoken of in this book as a **substance** or as a pure substance; it is homogeneous. If, however, it still contains a relatively very *small* quantity of any other component it is called an *impure* substance; any further treatment for the separation of such impurities is called *purification.* An impure 'substance' may be purified by crystallisation, distillation, and so on.

It must be noted, however, that to obtain a substance free even from minute quantities (*traces*) of impurities is generally a most difficult task; if the quantity of impurity does not exceed, say, 0·1 per cent., the properties of the substance, as a rule, are so slightly affected that for practical purposes it is considered to be pure. Most commercial substances contain more impurity than this.

In the methods described above for the separation of the components of mixtures, or for the purification of substances, the materials, in many cases, were changed in *state* (vaporised, dissolved, &c.), but not otherwise altered; such methods may be called *physical methods.* Later on it will be shown that such separations or purifications are often far more easily accomplished, or, indeed, can only be accomplished, by methods of a totally different kind, which are called *chemical methods.*

A substance having been purified in what may seem to be a suitable manner, how is it known that the substance is *pure?* By carefully examining it and ascertaining whether its *specific properties* are *constant.* If it is pure it is homogeneous, and cannot be separated into different *components*, or into two samples differing from one another in specific properties, by methods such as those described; if it is not yet pure it is still a mixture. Suppose that any pure substance is separated into two fractions by crystallising from water; these two fractions are *identical in every respect*—in melting-point, boiling-point, specific gravity, solubility, crystalline form, and so on; they have identical specific properties and physical constants. The samples might, of course, differ as regards the size of the crystals, and many of, or all, the crystals might be imperfect; but this is of no importance; they are both composed entirely of one and the same substance.

If, on the other hand, an impure substance were fractionally crystallised the two fractions would not be identical in every respect; that is to say, they would *differ* more or less in specific properties.

The term *material* has been used in these introductory chapters to denote any kind of matter, whether a mixture or a substance; henceforth it is employed, as far as possible, in the case of *mixtures* only.

CHAPTER V.

Some Common Substances.

In the great heterogeneous mass of matter forming the earth's crust a few substances occur in small quantities in a practically pure state; by simple processes, discovered in the course of time, others can be prepared from various 'raw materials.' A few such substances may now be very briefly described.

Copper, silver, mercury (quicksilver), and gold are found in various parts of the world in small quantities; iron, lead, and tin are prepared from natural materials (ores). These substances have been known from very early times, and used in daily life. They have certain properties in common: for example, all have a bright, shining appearance (*metallic lustre*); all may be melted; all have a high specific gravity; all are good conductors of heat and of electricity. On account of these *resemblances* they are classed together as **metals**; the word 'metal,' therefore, is the name of a class or group of substances. Although metals as a class have several common or general characteristics, the specific properties of every metal are different from those of any other form of matter; every metal * is a distinct substance.

Ordinary salt, 'common salt,' or **sodium chloride** is a well-known substance obtained in an impure state from mines (rock-salt), and also by the evaporation of sea-water (sea-salt); it is purified by recrystallisation, and is colourless and crystallises in cubes. When heated suddenly, the crystals often break up with violence and noise, because they contain enclosed drops of mother liquor (p. 32), which give rise to steam; this occurrence is known as *decrepitation.*

Nitre, saltpetre, or **potassium nitrate** is found in certain tropical and subtropical countries (India, Ceylon, Syria) in layers on the ground, and is purified by crystallisation from water; it is colourless, very readily soluble in hot water (its solubility is 247 at 100°), and melts when heated (m.p. 339°).

Soda-crystals, washing-soda, or **sodium carbonate** was originally obtained by burning seaweed, placing the 'ash' or residue in water, and allowing the clarified solution to evaporate spontaneously; it is now prepared by different methods (p. 274). The crystals deposited from the aqueous solution are colourless and transparent (like ice), but when they are left exposed to the air they gradually change into a white (colourless) powder, and lose in weight. If some freshly prepared crystals are carefully dried with blotting (filter) paper, and then heated in a glass tube, fitted up as shown (fig. 14),* they first liquefy and then begin to give steam, pure water collecting in the tube (*b*); after some time the contents of (*a*) begin to crystallise, and finally there remains a dry solid, which does not change on continued heating. When this solid is dissolved in the least possible quantity of hot distilled water, and the solution allowed to cool, crystals are obtained; these, when well dried with filter-paper, behave exactly like the original sample, and give water and a solid when they are heated.

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* Brass, solder, and other materials composed of two or more metals are called *alloys*. Brass is an alloy of copper and zinc, solder an alloy of lead and tin.

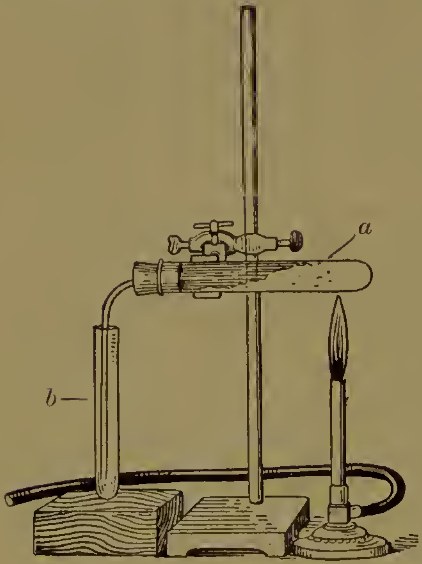

Fig. 14.

Blue vitriol or **copper sulphate** occurs in the drainage water from certain copper-mines, and when this solution is evaporated it gives crystals having the appearance of blue glass; hence the name blue vitriol (*vitrum*, glass) given to this substance. When these dry crystals are heated in an angle-tube (fig. 14) they gradually change, giving a colourless crystalline powder, and water collects in the tube (*b*). When the colourless powder is placed in a little water it turns blue, dissolves on warming, and the solution on cooling deposits crystals of blue vitriol *identical* with those of the original substance; the white powder also absorbs water, and slowly turns blue when it is left in the air (which shows that air contains water vapour).

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* This piece of apparatus is used so frequently that for convenience in reference it is termed an '*angle-tube*.'

Green vitriol or **ferrous sulphate** is a green glass-like crystalline substance, which is obtained on evaporating the drainage water from certain coal-mines. The crystals lose in weight and crumble when left exposed to the air, and when very *gently* heated* in an angle-tube (fig. 14) they yield water and a white powder; this powder is soluble in water, and from the solution crystals identical with those of the original substance are deposited.

Water of Crystallisation.—Dry crystalline substances, like sodium carbonate, copper sulphate, and ferrous sulphate, which give, or 'lose,' water when they are heated, generally do so at 100°, or at slightly higher temperatures; if, then, a known weight of the substance, carefully *dried* with filter-paper, is heated at a suitable temperature until constant (p. 23), the loss in weight gives the weight of the water which has been expelled. Such quantitative experiments show that for a given substance the percentage of 'water' contained in any *dry* sample is constant; thus soda-crystals always contain 62·9 per cent., blue vitriol 36·1 per cent., and green vitriol 45·3 per cent. of 'water' respectively.†

Now when materials such as *damp* nitre or *damp* common salt are heated at 100° they also lose water, but the quantity is *not constant*, and varies with the sample; further, in such cases the loss of water has no other result than that the material is *dried*. The water contained in such materials is termed *moisture*; its presence does not alter the form or other properties of the crystals. In the case of the crystals of soda, blue vitriol, and green vitriol not only is the percentage of 'water' constant, but its presence alters the crystalline form and other specific properties of the substances which contain it. The 'water,' moreover, is not in the

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* If strongly heated a different result is obtained (p. 39).

† In the case of green vitriol the percentage of water expelled cannot be determined in this simple way.

liquid but in the *solid* state. Water which plays this part is called *water of hydration* or *water of crystallisation*, and the crystals which contain it are said to be *hydrated*. Thus soda-crystals are composed of *hydrated* sodium carbonate; the crystals of a different form which are produced when the 'water' is driven off, or crystals such as those of nitre, sugar, &c., which do not contain 'water,' are termed *anhydrous;* the blue crystals of copper sulphate are hydrated, the colourless ones are anhydrous, and the conversion of the former into the latter is termed *dehydration*. Some hydrated substances undergo dehydration (partial or complete) even at ordinary temperatures, as, for example, soda-crystals; they are then said to *effloresce*, and are called *efflorescent*. Some anhydrous substances which can form hydrated crystals, as, for example, anhydrous copper sulphate, absorb and fix water (become hydrated) on exposure to damp air or when brought into contact with materials containing water or aqueous vapour; such substances are called *hygroscopic*, and are often used for abstracting water from different materials—that is to say, for drying them. Some hygroscopic substances, as, for example, *calcium chloride*, thus absorb so much water that they dissolve in it; they are then said to *deliquesce*, and are called *deliquescent*. The liquid produced by quickly heating soda-crystals is not melted sodium carbonate, but a concentrated *aqueous solution* of this substance; hydrated substances which behave in this way are said to dissolve in their water of hydration; anhydrous sodium carbonate only melts at a very high temperature (red heat).

Substances containing water of crystallisation are not regarded as *impure;* but water (moisture) adhering to anhydrous or hydrated crystals is merely impurity. Other solvents besides water may be fixed in crystals.

Salts.—The four substances 'common salt,' nitre, blue vitriol, and green vitriol have certain properties in common; they are all solid, crystalline, and transparent. For these and also for other far more important reasons, which will be explained later, they are classed together as *Salts*, so that the term salt, like that of metal, is a class-name given to a great number of different substances. Many salts have been known from very early times, and by simple processes other substances have been prepared from them.

When crystals of green vitriol are heated very strongly in an angle-tube (fig. 14) choking fumes* are given off, and the residue gradually becomes red; if the fumes are passed into a test-tube (*b*) containing a little water they dissolve, and the solution acquires a sour or 'acid' taste.† When some of this solution is evaporated in a basin heated on a sand-bath it becomes thick and oily; this liquid is called oil of vitriol, and the 'acid' substance contained in it is known as **sulphuric acid.** The red powder which remains in the tube is insoluble in water, and absolutely different from green vitriol in other properties; the change which has occurred is of a different type from any yet considered.

When a mixture of green vitriol and nitre is heated in a retort a brown gas or vapour is produced, and there distils a yellowish fuming* liquid, at one time called 'spirit of nitre,' but now known as **nitric acid.** Pure nitric acid is colourless, very corrosive, and has a sour taste.† The solid material remaining in the retort is *not* nitre or anhydrous ferrous sulphate, and the change which has taken place is very different from any already studied.

When oil of vitriol is heated with common salt a fuming gas is obtained; if this gas is passed into water the liquid becomes sour and sharp in taste. Such a solution, at one time called 'spirit of salt,' is now known as **hydrochloric acid.** The residue is not sulphuric acid or common salt.

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* Fumes or mists consist of very small particles of liquid (or solid); the visible mist escaping from boiling water (often wrongly called steam) is composed of drops of liquid water.

† These 'acids' can only be tasted safely when they have been diluted with a large volume of water. Great care should be taken that acids and 'chemicals' generally do not get on to the skin, and danger to the eyes should be most carefully avoided.

Sulphuric acid, nitric acid, and hydrochloric acid have certain properties in common; all have a sour taste;* all are corrosive—that is to say, they eat into and burn or spoil many materials, such as cloth, wood, skin, and many *metals.* The term '**acid**' is thus used as a class-name, and is applied to a great number of substances having certain properties in common. The three acids named above are prepared in chemical-works on the large scale.

The presence of an acid in an aqueous solution can often be ascertained by adding a solution of *litmus.* Litmus is a blue material prepared from certain lichens, and is soluble in water; when its aqueous solution is added to an acid the blue material (blue litmus) is turned into a red one (red litmus). Papers soaked in a blue or red litmus solution and then dried are known as *litmus-papers.*

CHAPTER VI.

Chemical Change.

It has now been shown that when a substance is heated it may undergo a change in state; it may melt; it may vaporise. In such cases, moreover, when the conditions are reversed the changes are *reversed;* the substance is then exactly as it was at first, except perhaps in shape; it still exists or endures, and has done so all the time in one state or the other. Such changes may be referred to as *physical changes,* and strictly speaking the study of such changes is rather a branch of physics than of chemistry.

It has also been shown that many substances may be dissolved; this change also is reversible, for by evaporating the solvent the substance may be recovered unchanged, except perhaps in shape.

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* Compare footnote, p. 39.

Again, some substances may be hydrated—that is, they may form, with water, dry, homogeneous crystals of fixed composition; this change also is reversible, as the water of hydration may be expelled by heating. Is a substance which is dissolved or hydrated merely *mixed* with the solvent? If so these changes may also be called physical changes, by which is understood changes which only alter the state or condition of a substance, but not its specific properties.

It is clear, however, that some of the changes referred to in the last chapter are of an entirely different kind, namely, those which occur on heating (1) ferrous sulphate, (2) a mixture of nitre and ferrous sulphate, (3) a mixture of salt and sulphuric acid. In these changes, which are examples of *chemical change*, the original substances disappear and new ones having totally different specific properties are obtained. Some further examples of chemical change may now be studied in a systematic manner.

Copper Heated in the Air.—When a sheet of bright copper foil or gauze is heated in a Bunsen-flame it changes colour and finally becomes black. This blackening is not due to soot, for if the sheet be heated on one side only, both are blackened; if the surface is scraped a black powder comes away and bright metal is exposed, but on heating again more black substance is formed on the bright parts. What has happened? The black substance does not change again into copper when it is cooled. Has some of the metal burnt, or changed into something which has escaped into the air?

Copper Heated in an Enclosed Space.—In order to find out whether anything comes away from the copper while this black substance is being formed a roll of the bright metal * is heated in an angle-tube (*a*, fig. 15), the outlet (delivery) tube of which dips into some water contained in the vessel (*b*). At first a few air-bubbles escape from the tube; but it is known that this would happen even if there were no copper there, because air expands when it is heated (p. 158). After heating for some minutes it is found not only that nothing escapes from the tube, but also that the metal is hardly changed and does *not* give a black substance. Why doesn't it? Has it not been made hot enough?

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* The metal should fill the tube as far as possible; the roll is obtained in a bright condition by making it red-hot in a blowpipe flame and immediately placing it in a large test-tube which contains about 2 c.c. of alcohol.

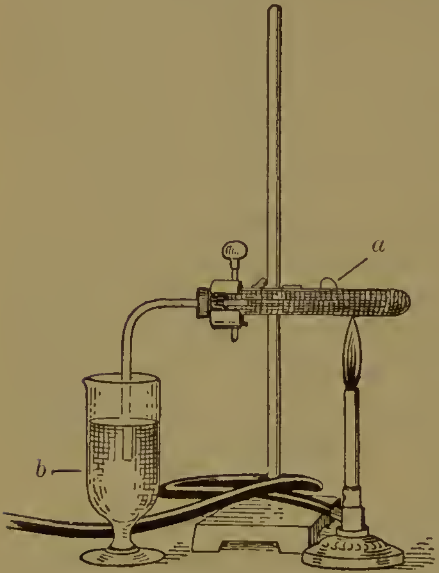

Fig. 15.

No very noticeable change occurs however long the metal is heated in this way. If, however, the cork is taken out of the tube, while keeping the copper hot, that part of the metal near the open end of the tube gradually turns black, although it is not being heated any more strongly than before; slowly the metal becomes black all over.

From these observations it might be concluded that the air causes this blackening. When the copper is heated in a tube containing a very little air and no more air is allowed to get to it, the metal is hardly changed perceptibly; when, however, air gets to the metal the black substance is obtained.

Copper and Nitric Acid.—When some copper is put into water it does not dissolve, and is not changed in any way; but when the metal is placed in nitric acid,* some remarkable changes take place very quickly. A fizzing or effervescence is noticed; a brown vapour or gas appears; the liquid becomes blue and gets hot; finally all the copper disappears, and instead of colourless nitric acid and the metal copper, there appear now a blue liquid and a brown gas (most of which has escaped into the air). When some of this blue liquid is evaporated on a water-bath, there remains a blue crystalline substance, which is called *copper nitrate;* this salt is readily soluble in water.

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* Compare footnote, p. 39, on the dangerous character of nitric acid.

Now contrast the behaviour of sugar, common salt, or blue vitriol dissolving in water with that of copper when it is put into nitric acid. How great are the differences! When one of the former is dissolved in water no gas is formed, no visible change occurs except that called solution, and the dissolved substance may be recovered unchanged by evaporating the solution; the imagination may picture the substance as still existing, although in solution. In the case of copper and nitric acid at least two new substances, viz. a brown gas and a blue solid, are obtained; *copper* is not recovered on evaporating the solution, and the imagination cannot picture the metal as still existing as such.

If, then, it were said that copper *dissolves* in nitric acid, or that copper is soluble in nitric acid, these terms would be used to express processes very different from those to which they have already been applied. The copper is obviously changed by the nitric acid, but not merely in *state;* and the result is a solution, *not* of copper, but of the substance *copper nitrate.*

When, therefore, the substance which passes into solution is different from that which is put into the liquid the process may be called *chemical* solution, and the original substance may be said to dissolve chemically.

Copper Nitrate Heated.—When copper nitrate is heated considerably above 100°* the blue solid begins to change. First it seems to melt (but is really dissolving in its water of crystallisation, p. 38); later on a brown gas is given off and a black substance begins to form; finally the blue solid disappears entirely, and there remains a dry, black powder

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* This process is generally called 'ignition;' any material heated strongly in a vessel is said to be 'ignited' even if it undergoes no change.

which does not change visibly on further heating. This black powder is insoluble in water; when put into nitric acid it gives a blue solution, but no brown gas; when this solution is evaporated there remains a blue crystalline solid which can be identified as copper nitrate, and which when heated gives (of course) the black powder and brown gas.

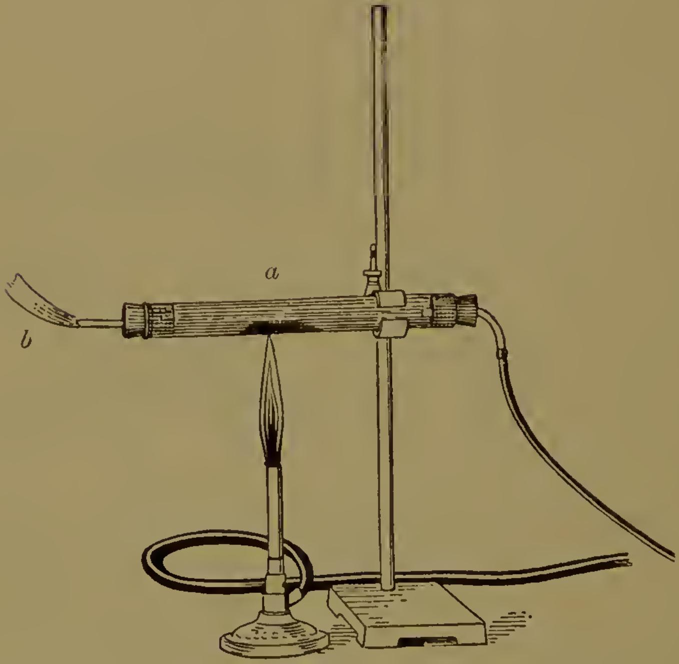

Fig. 16.

The Copper Reappears.—When the black powder obtained by heating copper nitrate is placed at (*a*) in a glass tube (fig. 16) through which coal-gas is passing, the black powder does not undergo any visible change. If now (after lighting the gas escaping at (*b*) and turning the flame very low) the powder is gently heated with the Bunsen-flame, it changes in a remarkable manner, and gives a reddish or salmon-coloured solid substance. Careful observation may also lead to the discovery that some *liquid* condenses in the colder portions of the tube, although the powder may have been made red-hot (and therefore must have been quite dry) before it was used.

The red powder thus obtained does not *look* very like ordinary copper, but when examined it is found to have the following properties: (*a*) When hammered on an anvil (or melted and cooled) it gives a coherent mass which has the colour and lustre of ordinary copper,* the same specific gravity as copper, the same melting-point, and so on. (*b*) It blackens when it is heated in the air; when placed in nitric acid it behaves just as copper does, and gives a blue solution from which blue crystals, black powder, and red solid can be obtained in turn by the methods just described. In short, it is found, by *every test* that can be applied, that this red powder *is* copper. It is identified as copper not merely by its physical properties (*a*), but also by those (*b*) of another kind, namely, its *chemical properties*, some of which are noted above.

From these experiments it may be concluded that both the blue crystals (copper nitrate) and the black powder contain the stuff or matter which is called copper; but in these substances the metal is in a condition so different from that of ordinary copper that it cannot be recognised. Also, that there is something in coal-gas which is not in air, or why should the black powder change and give copper when it is heated in coal-gas?

Copper Carbonate.—When copper nitrate is dissolved in water and a solution of sodium carbonate (p. 35) is added, pale-blue solid particles are *precipitated* or thrown out of solution; on adding sufficient sodium carbonate solution and pouring the whole on to a filter the blue *precipitate*, which is called *copper carbonate*, can be separated, and the filtrate is colourless. The precipitate is *washed well* and dried in the steam oven.

On heating copper carbonate in an angle-tube (fig. 15), with the outlet dipping under water contained in (*b*), bubbles of gas rise through the water, and the blue substance begins to turn black; far more gas escapes from the tube than could be due to the expansion of the air, and finally instead of copper carbonate there remains a black powder.

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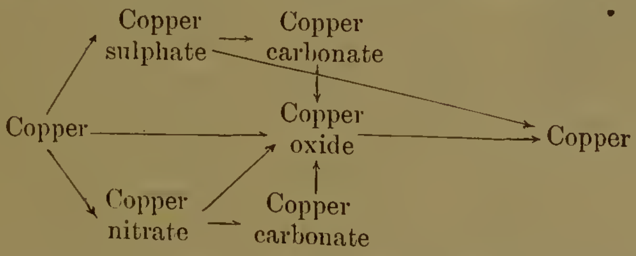
* This is an instance of how the appearance of a substance may alter with its state of division.

Copper Oxide.—A black powder has now been prepared in three different ways: (1) by heating copper in the air, (2) by heating copper nitrate, and (3) by heating copper carbonate. Are these 'preparations' the same or different substances? Experiments show that by whichever method this powder is prepared it has the same physical and chemical properties. The *identity* of the three 'preparations' or samples is easily proved by tests. For example, all are insoluble in water; all have the same specific gravity; all give copper nitrate with nitric acid; all give copper when heated in coal-gas. This black substance is called *copper oxide.*

Copper Sulphate.—When copper oxide is warmed with sulphuric acid (p. 39) diluted with water, a blue solution is obtained but no gas is seen. On evaporating this solution there remains a blue crystalline solid, namely, blue vitriol or copper sulphate, which is a different substance from copper nitrate, as can be easily shown by heating it in a hard glass tube; instead of turning black and giving a brown gas (p. 43) it turns white, giving water (p. 36). Blue vitriol may also be obtained by heating copper with sulphuric acid (p. 39). Copper may be obtained from blue vitriol in various ways. A solution of sodium carbonate may be added to a solution of blue vitriol; this causes the precipitation of copper carbonate, from which copper oxide can be prepared first, and then the metal, as just described. Again, when a bright piece of iron (or steel) is placed in the solution of copper sulphate, that part of the iron which is covered by the solution becomes salmon-coloured; it then looks very like the copper obtained by heating copper oxide in coal-gas, and it can be proved in many ways that the outside layer *is* copper. Has the iron been changed into copper? After some time, using enough iron, the solution loses its blue colour entirely, so that the blue vitriol must have changed; it may be concluded, therefore, that the coating of copper on the iron has come from the blue vitriol.

From the experiments with copper which have now been described, it will be seen that many substances may undergo changes quite different from those in which they merely change in state or dissolve. One substance seems to change into or become something quite different. A bright, shining metal gives a black powder, also several blue substances quite different from one another; from all these blue substances one and the same black powder, and finally one and the same metal, can be again obtained. These are further examples of *chemical change*, and they are summarised diagrammatically below; the arrows point towards the substance which is formed under conditions described above, but it must be carefully borne in mind that *in every case*, excepting the direct formation of copper oxide by heating the metal in the air, other substances are produced as well as those here shown.



Some Chemical Changes examined Quantitatively.

Some of the qualitative experiments with copper which have just been described may now be considered quantitatively, and in the first place the change which occurs when copper is heated in the air may be examined. In order to find out whether the metal gains or loses something a roll of clean copper gauze* is weighed, then heated in the air for some minutes, allowed to cool, and weighed again.

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* Footnote, p. 41.

The result of this experiment will show that there is a *gain* in weight, and therefore the formation of the black powder is not due to anything leaving the copper, but to something having weight being added to it. This matter must have come from the air, a conclusion which confirms the result of the qualitative experiment (p. 42).

On heating, cooling, and weighing the roll again, a further increase in weight would be found, and a similar result would be obtained even after many repetitions of the experiment. This is not surprising, because, as already shown, the black powder forms at the surface of the metal, and the air gets to the lower layers very slowly.

As it would take hours of heating to finish the change under these conditions, the black powder may be prepared from the metal by one of the other methods.

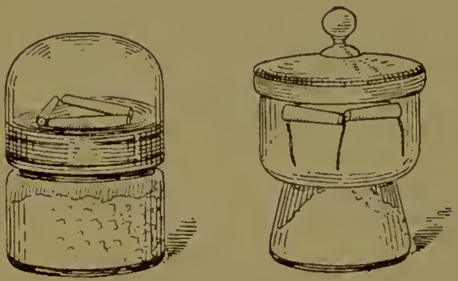

Fig. 17.

A weighed quantity (about 1 gram) of copper is placed in a weighed crucible, and nitric acid (enough to change all the metal into copper nitrate) is carefully added; the solution of copper nitrate is then evaporated to dryness, and the residue strongly heated; when cold * the crucible and copper oxide are weighed. The result would be something like this:

Weight of copper . . . . = 1·0030 g.
" copper oxide . . . = 1·2557 g.

Increase in weight = 0·2527 g.

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* Copper oxide is very hygroscopic (p. 38). In order to prevent it from taking up aqueous vapour from the air, the crucible is cooled in a vessel containing dried air, called a 'desiccator' (fig 17). The desiccator contains some very hygroscopic substance, such as calcium chloride (p. 38) or sulphuric acid.

The crucible and contents are again heated and again weighed (until constant *); if the experiment has been well done, the second weighing gives the same result as the first.

Since 1·003 g. of copper give 1·2557 g. of copper oxide, by proportion, 100 g. of the metal give 125·2 g. of oxide, or 100 g. of oxide are obtained from $\frac{100 \times 100}{125 \cdot 2} = 79 \cdot 9$ g. of the metal.

Now if this experiment were repeated many times, weighing very accurately, taking extreme care not to spill any of the copper, or blue solution, or copper oxide, and making sure that the latter did not contain any moisture or blue solid—in short, if the experimental error (p. 24) was very small, the average result of any set of experiments would always be that given above. This fact has been proved by a large number of experiments carried out by skilled chemists.

Further, it does not matter by which of the several processes described above the copper oxide is prepared, the result is *always the same* within the limits of experimental error; that is to say, unit weight of copper always gives 1·252 units of copper oxide. This last statement confirms a previous conclusion, namely, that the black powder obtained by different methods is one and the same substance.

The weight of copper obtained from a known weight of copper oxide may now be determined by heating a known weight of the carefully dried substance in a stream of coal-gas as already described (p. 44), and weighing the metal obtained. The substance is weighed in a porcelain 'boat,' which is put at (*a*) in the tube (fig. 16); coal-gas is passed through the tube, the oxide is heated until no further change occurs, and the metal is allowed to cool and weighed. The result would be something like this:

Weight of copper oxide . . . . =0·7846
" copper . . . . . =0·6269

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* Compare footnote, p. 23.

Since 0·7846 g. of copper oxide gives 0·6269 g. of copper, 100 g. of the oxide give $\frac{0{\cdot}6269 \times 100}{0{\cdot}7846} = 79{\cdot}9$ g. of metal.

Skilled chemists carrying out this experiment with the greatest care have *always* found the average result to be that just given, and it does not matter by which of the processes described above the copper oxide is prepared, the result is always the same.

It is thus proved that when copper undergoes change, giving copper oxide, 79·9 g. of metal give 100 g. of the oxide (p. 49); and that when copper oxide undergoes change, giving copper, 100 g. of the oxide give 79·9 g. of the metal.

Starting, therefore, from a given weight of copper, a number of different substances may be obtained, and finally the metal may be recovered. The weight of the recovered metal is exactly the *same* as that of the metal taken; but, as can be proved by quantitative experiments, the weight of every intermediate substance is *greater* than that of the metal used.

It is thus proved by these qualitative and quantitative experiments that when copper nitrate is heated, it is broken up or changed into (at least) two other substances, viz. copper oxide and a brown gas; also that when copper carbonate is heated it is broken up into (at least) two other substances, viz. copper oxide and an invisible gas; such changes are spoken of as *decompositions*, and the copper nitrate or copper carbonate is said to be *decomposed*. Copper oxide must also give something besides copper when it is heated in coal-gas, as the change involves a loss in weight; this decomposition is studied later (p. 105).

The results of all these experiments with copper lead to the following conclusions:

(1) When copper is changed so that it is no longer copper it is because something having weight is added to it.

(2) When such a change occurs, the copper takes up a

fixed quantity of some other matter, and loses this same fixed quantity when it passes back into copper.

(3) Copper cannot be destroyed or annihilated or caused to pass into nothing—not even the smallest particle of it.

CHAPTER VII.

Elements and Compounds.

Many of the substances which are classed as metals (p. 35)—as, for example, iron, lead, tin, mercury, aluminium, zinc, magnesium, silver, gold, platinum—have been known for a very long time, and have been very carefully examined by chemists in all sorts of ways, of which the experiments with copper may give some idea. It has thus been found that although metals may be changed by adding some matter to them, they cannot be broken up or decomposed into two or more *different* substances, as can copper nitrate, copper carbonate, or copper oxide. A metal cannot be changed by taking some matter from it.* Such substances are called elementary substances, or **elements.** An element is a distinct kind of matter which has never been decomposed to the knowledge of the chemist; it may be changed in state, and it may also be changed by adding something to it, but it cannot be destroyed.

It must not be supposed that metals are the only elements; about eighty elements are known, but the only ones in addition to the metals which are commonly *seen* are sulphur, iodine, and carbon, and possibly phosphorus. Some of the elements are *invisible* gases.

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* How is it known that the gas which is produced when copper is placed in nitric acid does not come from the metal? Although the metal increases in weight, this might be because it gained more matter from the acid than it lost as gas! In answer to such a question it may be stated that this gas is never obtained from the metal except with nitric acid, and the gas can be obtained from nitric acid without using copper. Further, the *quantitative* experiments prove that the *whole* of the copper can be recovered from the solution without adding the gas again.

Returning now to the element copper, it has been shown that when this metal is heated in the *air* it adds to itself something in the air; this something is an invisible gas, an *element* called *oxygen*, and in taking it up not only the copper, but also the gas is absolutely and entirely changed.

Now copper oxide cannot possibly be regarded as a *mixture* (p. 27) of copper and oxygen, and it is called a **compound** of the elements copper and oxygen. Why the elements become so different when they form the compound is not known, but in order to indicate the fact that the elements copper and oxygen are not merely mixed together, they are said to have **combined** or united together chemically, and the change which occurs during their combination is called a *chemical change*. Copper nitrate, copper carbonate, and copper sulphate are also *compounds;* but in each of these substances the element copper is combined with *two* other elements, as will be shown later.

It would be useless to attempt to define chemical change at present, but it may be pointed out that nearly all the changes dealt with in Chapter VI. belong to this class. The decomposition of a compound, such as copper carbonate, into two or more different substances (elements or compounds); the separation of the element copper from the compound copper oxide; the formation of copper nitrate from copper and nitric acid, &c., are all examples of chemical change. In all these cases the substance or substances resulting from the change are entirely different in specific properties from those which take part in it; this is a general characteristic of chemical change.

There is another most important characteristic of chemical change which has already been illustrated. When copper is changed, giving copper oxide, it combines with a fixed quantity of some other matter (oxygen), and loses this same fixed quantity when it again passes into copper. No matter how the compound copper oxide is made, it always contains or is composed of 79·9 per cent. of copper and 20·1 per cent. of oxygen (p. 79); it is a substance of *fixed and definite composition.*

This does not mean that if a strip of copper is heated in the air, say for five minutes, until it is outwardly black all over, the strip then contains 20·1 per cent. of oxygen. Of course it will not; it will not be copper oxide, except just near the surface, but a heterogeneous mixture of copper and copper oxide. *Pure* copper oxide is not only a substance of fixed and definite properties but of fixed and definite composition.

Now experiments with hundreds or thousands of (pure) compounds have shown that each has a fixed and definite composition; it is therefore concluded that this is true of every compound, and so this general conclusion becomes a law—**the law of definite proportions.**

The proportion of each element present in a chemical compound is fixed and constant.

When chemical change occurs the *relative* quantities of the substances which take part in the change, which combine with or *act on* one another, are fixed and constant.

It follows from this law (which it must always be borne in mind is based entirely on experiment) that if two samples supposed to be one and the same compound are found to differ in composition, one or both *must be impure;* also that the determination of the composition of a compound serves for its identification. If a given black powder of unknown origin were found to contain only 79 per cent. of copper it could not be *pure* copper oxide; whereas if it were found to consist of 79·9 per cent. of copper and 20·1 per cent. of oxygen it must be copper oxide, since no other substance has this composition.

The law of constant proportions also renders it possible to calculate how much copper oxide would be obtained by converting any given weight of the metal into copper oxide, or how much copper could be obtained from any given weight of copper oxide. An example will make this clear.

How much copper oxide can be obtained from 0·3280 g. of copper? Since this compound consists of 79·9 per cent. of copper and 20·1 per cent. of oxygen, 79·9 g. of copper give 100 g. of copper oxide. By simple proportion, therefore, $79{\cdot}9 : 0{\cdot}3280 :: 100 : x$; the result is 0·4105 g. This result *of course* would be confirmed by an actual experiment, because it is based on experiments previously made.

As a matter of fact the law of constant proportions has already been assumed in calculating the percentage composition of copper oxide; for if this compound were not constant in composition, 100 g. of metal would not necessarily give 100 times as much copper oxide as 1 g. of metal. The calculation of the *percentage* of water of hydration (p. 37) from the experimental data is also based on this law.

Returning once more to the quantitative experiments, it was concluded (3, p. 51) that copper cannot be destroyed or annihilated; something may be added to it, combined with it, and again taken away from it, but it is impossible to 'destroy' it—the same mass of *copper matter* always remains. What is true of copper is true of every element, and therefore of every compound, because compounds are composed of elements.

These facts are summarised in **the law of the indestructibility of matter** (conservation of mass). *Matter may be changed in state, or may undergo chemical change, but its mass remains constant; it cannot be destroyed, nor can it be created.*

This law has been established by innumerable experiments, and the whole science of chemistry is based on it. If it were not true, quantitative experiments would be useless and calculations such as those given above impossible. What would be the object of starting such an experiment with a weighed quantity of copper or copper oxide if some of the matter might pass into nothing during the experiment?

Putting this law in another way, 'when changes in state, or chemical changes, or both occur, the sum of the weights of the original substances is identical with that of the weights of the products (or substances obtained).'

Many simple experiments may be shown as demonstrations of this law. A beaker containing some water and a glass rod is placed on one pan of a balance together with some washing-soda on a watch-glass and some blue vitriol on a watch-glass, and the whole is counterpoised; the blue vitriol is first dissolved in the water, and then the washing-soda, the solution being stirred with the glass rod. Physical and chemical changes have then taken place; the two solids have first been dissolved, and have then been chemically changed, but the sum of the weights of the products is exactly the same as that of the original substances.

The meaning of the word compound as used in chemistry should be very clearly understood. A compound is a substance which is known to be composed of at least two elements; it may contain three or more. Two elements merely side by side are not a compound but either a mixture or a solution. The nature of mixtures and of solutions has already been considered; the components retain their own specific properties and exist side by side, a slight variation in their relative quantities does not alter the properties of the mixture or solution perceptibly, and there is nothing fixed and definite about its composition. The *constituents* of a compound do not retain their own specific properties; they combine together in fixed proportions, forming a homogeneous substance having properties totally different from those of its constituents.

It does not necessarily follow that the components of a mixture are more easily separated from one another than are the constituents of a compound; it is far more difficult, for example, to separate the components of the heterogeneous mixture known as granite than to obtain copper from the homogeneous compound copper oxide.

But there is this very important difference between mixtures and compounds: the former *may* possibly be separated into their components by simple physical processes which only cause changes in state (p. 33); the latter can *never* be resolved into their constituents by such methods, but must be *decomposed;* that is to say, they must undergo chemical change.

Chemical methods are also far more generally useful than the simple physical methods already described for the separation of the components of a mixture. Thus a mixture of sand and copper powder could be separated into its components by placing the mixture in nitric acid, in which sand is insoluble. As soon as all the copper had been chemically changed into copper nitrate, the solution would be filtered (p. 22) and the residue of sand washed with water (p. 30); the copper could then be recovered, as metal, from the filtrate by one of the methods already described. If these operations were carried out in order to identify the components of the mixture, the process would be called a *qualitative* (chemical) *analysis;* if the quantities of the components were also determined, the operation would be a *quantitative* (chemical) *anaylsis.*

The *identification* of a substance is also, generally speaking, most conveniently carried out by examining its *chemical* properties—that is to say, by studying the definite or specific changes which the substance undergoes when it is brought into contact with other substances under certain *fixed* conditions. Thus it is much easier to identify copper by placing it in nitric acid and thus obtaining a blue solution, which on evaporation, and ignition of the residue, gives a black powder, and so on, than by determining the melting-point or specific gravity of the metal.

The chemical properties of a substance, although generally so 'characteristic' (that is to say, different from those of other substances), cannot be regarded as attributes of the substance *itself,* but rather as those of a conjunction or *system* of two (or more) substances; thus the formation of the compound copper oxide is just as much a property of oxygen as of copper.

CHAPTER VIII.

Limestone, Chalk, Marble, and Calc-Spar.

The gray 'rock' *limestone* occurs in enormous quantities in the earth's crust, forming in some districts huge mountain-ranges. On examining some pieces of limestone, shells and fossils may be seen embedded in it, and it is probable that the great deposits of limestone in different parts of the world have been formed from the remains of once living things. Although the presence of such fossils does not necessarily make limestone a mixture, from a chemical point of view, it seems unlikely that a material so produced should be all the same *substance*.

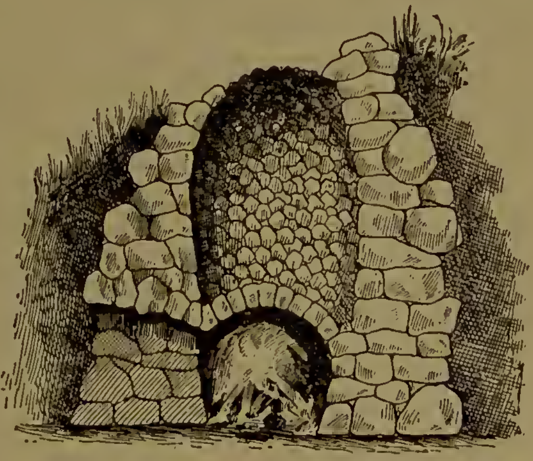
Fig. 18.

Limestone has been used from the very earliest times, and is used still, in making *quicklime*. For this purpose lumps of limestone are packed into a limekiln as shown (fig. 18), and a fire is then made in the chamber below. The limestone does *not* burn (although the process is often called lime-burning), but is merely strongly heated; when the fire has died down, the kiln is allowed to cool and the contents are then drawn out.

The product, quicklime, is still in lumps, showing that the limestone has not been melted, and looks very like the original material; when, however, water is slowly poured on pieces of limestone and of quicklime, a great difference in behaviour is noticed. The water merely runs off the limestone; the quicklime sucks the water up, as does a dry sponge, and is evidently very *porous*. As much *cold* water having been added as the quicklime will rapidly absorb, it is seen that after some time, which varies greatly with different samples, the quicklime begins to steam, and cracks, often with considerable violence.* These changes gradually become more noticeable, and finally, instead of a lump of quicklime, there remains a bulky, dry, hot powder—so hot, indeed, that a little gunpowder or a few lucifer-matches thrown on to it may take fire. This process is called 'slaking' the quicklime, and the product is called *slaked lime.*

It is clear that the limestone has been changed in the kiln. What has happened to it? Has it lost water of hydration (p. 38), or has it taken up something from the air, as copper does (p. 48), or something from the coal? Quantitative experiments show that limestone does not take up anything when it is strongly heated alone in a crucible over the blowpipe flame (p. 7); in fact, a distinct *loss* in weight occurs. As no *visible* change takes place, it seems that something invisible escapes. How can it be known when the change is complete? By heating until the weight becomes *constant* (p. 23). The result of such an experiment shows a loss in weight of, say, 43 to 44 per cent., and the product seems to be identical with quicklime produced in the ordinary way, since it gets hot and gives a dry powder when a little cold water is poured on it.

Is the loss in weight due to the escape of water vapour?

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* Care should be taken that pieces do not fly into the eyes.

If so, slaked lime might be identical with limestone. How can it be ascertained whether these two materials are identical or not? By examining their specific properties.

Now limestone seems to be insoluble in water; slaked lime also does not *seem* to dissolve. When, however, quantitative experiments are made (as with common salt, p. 23), it is found that there is *some* difference between the two. Distilled water which has been saturated with limestone at ordinary temperatures (and then filtered) does not give any appreciable residue (only 0·001 g. from 100 g. of solution), but the residue obtained from the same quantity of a filtered saturated solution of slaked lime is about 0·17 g. Although these solubilities are very small, if it were known that the limestone and slaked lime were both *pure* substances, and that there really was this difference in solubility, this fact would be sufficient to *prove* that the two substances are not identical; but bearing in mind that limestone is a natural mineral, which has not been purified (p. 33), and which might be a heterogeneous mixture, the larger quantity of soluble material obtained from the slaked lime might be nothing but some chance impurity in the particular sample of limestone from which the slaked lime had been made.

A very curious difference between limestone and slaked lime, however, would almost certainly be observed in making these solubility determinations—namely, that the water filtered from the former remains clear, while the clear solution of the latter becomes turbid (milky) on keeping it in an open vessel, owing to the separation of a white solid substance. The reason of this will be considered later.

The results of these experiments having been inconclusive, the limestone and the slaked lime may be examined or 'tested' in some other way; for example, their behaviour with hydrochloric acid * (p. 39) may be studied.

Now when limestone and slaked lime are placed separately in this acid, both rapidly disappear; but whereas a great deal of bubbling (effervescence) is observed in the case of the limestone, there is none in the case of the slaked lime.* The escaping bubbles consist of an invisible gas. Does this gas come from the limestone or from the hydrochloric acid? As limestone loses something when it is changed to quicklime, and as neither quicklime nor slaked lime gives any gas with hydrochloric acid, it seems reasonable to conclude that the matter which is lost when limestone is heated is the same invisible gas as that which causes the effervescence. In order to try to settle this point, some powdered limestone is strongly heated with the blowpipe flame (p. 7) in an angle-tube † (fig. 15, p. 42); it is then found that a gas *is* given off, and in consequence there is of course a loss in weight.

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* The commercial acid is 'diluted' with 4 to 10 volumes of water before use in these experiments.

Now as limestone can hardly be a mere *mixture* of quicklime and gas, it is probably a *compound*, or at any rate it contains a compound (there is no evidence yet that it is not a mixture of two or more compounds) which is broken up or *decomposed* at a high temperature.

Leaving the inquiry at this stage, some properties of certain other white or gray materials which are found in the earth may be considered. Of these *chalk* is one of the best known. It is found in huge beds in various parts of the world (e.g. the cliffs of Dover), and is generally white and softer than limestone; it is friable and will rub off on to the fingers. When examined under the microscope it is seen to consist of fossil remains of very small marine animals (foraminifera), and it is believed that all the immense deposits of chalk were originally formed under water by the accumulation of these animal remains.

When chalk is strongly heated it loses in weight (43 to 44 per cent.), a colourless gas escapes, and the product is a colourless solid which behaves like quicklime; chalk, like limestone, is insoluble in water, but it dissolves chemically in hydrochloric acid with effervescence. From this similarity in chemical properties, it might be concluded that chalk and limestone are the same compound, or at any rate contain the same compound.

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* If the quicklime has not been properly prepared the slaked lime will contain some limestone, which *of course* will cause some effervescence.

† A silica tube (p. 293) may be employed in this experiment.

Marble is another material well known by sight; generally white, sometimes brown or black, it often *looks* heterogeneous, and is marked with veins and with patches of different shades; it is harder than chalk or limestone, and can be polished; when a piece is broken, the rough surface (fracture) glistens in parts and seems to be *crystalline*.

When marble is strongly heated it loses in weight (43 to 44 per cent.) and an invisible gas escapes; the residue, although it may not always *look* like quicklime, behaves like the latter when water is added to it. Marble is insoluble in water, but it dissolves chemically in hydrochloric acid with effervescence. From these facts it might be inferred that marble is, or contains, a compound identical with that present in limestone and chalk.

Gypsum, kaolin (or China-clay), and many other materials which look rather like marble or chalk are found in the earth, but examination shows at once that they differ from limestone, chalk, and marble in properties; thus when gypsum or kaolin is heated, it merely loses water (no gas) and the residue is quite different from quicklime; further, gypsum and kaolin do not give a gas when placed in hydrochloric acid.

In limestone districts there is often found a beautiful mineral which is called *calc-spar*, *calcite*, or *Iceland spar*; this mineral forms glistening transparent *crystals*, and *looks* very different from limestone, chalk, and marble. And yet it behaves, chemically, very like them. When strongly heated it loses in weight and gives quicklime; when placed in hydrochloric acid it disappears and gives an invisible gas.

Now as calc-spar is crystalline and therefore probably a *pure* substance, it may be used for some further quantitative experiments; it hardly seemed worth while to make many such experiments with limestone, &c., as the purity of the materials was so very doubtful.*

Such experiments show that when calc-spar is heated until constant, it loses 44·0 per cent. in weight and gives 56·0 per cent. of quicklime. *Different samples* of calc-spar from various parts of the world can be easily identified by their crystalline form and other properties; experiments show that *every* sample of calc-spar loses *exactly* 44 per cent. of gas and gives *exactly* 56 per cent. of quicklime. It is thus proved that calc-spar is a compound and that it is *pure*, otherwise it would not have a *fixed composition.* Different samples of limestone, chalk, or marble do *not* give a fixed loss in weight, but the percentage varies from, say, 43 to 44; therefore, although qualitative and quantitative experiments show that these materials probably consist almost entirely of the same compound as calc-spar, yet if so, they must be impure. Hence it might be inferred that the difference in colour between white, brown, and black marble is due to the impurities.

CHAPTER IX.

Carbon Dioxide.

The gas which is given off, *evolved*, or *liberated* when limestone, chalk, marble, or calc-spar is placed in hydrochloric acid may now be studied.† For this purpose some lumps of limestone are placed in a Woulff's bottle fitted up as shown (fig. 19) with *thistle funnel* (*a*) and *delivery-tube* (*b*), the free end of the latter passing through a '*beehive*' (*c*)* which is immersed in water contained in a suitable basin (*pneumatic trough*). A little water is first poured in, until the lower end of the thistle funnel is covered, and then some hydrochloric acid; the gas which is liberated mixes with and gradually drives out the air in the flask. When, judging by the volume of gas which has escaped, most of the air has been expelled, a glass cylinder (gas-jar) filled with water is closed with a glass plate, placed upside-down on the

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* Even if limestone were a very heterogeneous mixture (p. 27), it would be possible, of course, by merely grinding it to a fine powder to obtain a sample sufficiently 'intimate' to give constant results. But such results would not have any *general* value, because other samples of limestone from different portions of the rock material would probably give different results.

† One of the commonest operations in chemistry is to bring one substance (solid, liquid, or gas) into contact with another in order to obtain one or more new substances. This may be done in various ways, and the result may depend entirely on the conditions under which the experiment is carried out. When, however, it is unnecessary to specify these conditions and a mere bringing together gives the desired result, the one substance is

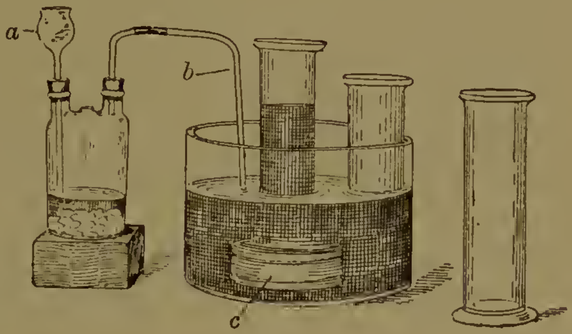

Fig. 19.

said to be 'treated with' the other. The question may then arise, what quantities of the different substances are to be used? For example, how much limestone and how much acid should be taken in preparing this gas?

Obviously this depends on the quantity of gas required; since limestone gives an approximately constant quantity of gas, more than this cannot be obtained from it. If, then, a small piece, say 2 g., is taken to start with, a rough idea of the volume of the gas obtained from it, using sufficient acid, may be formed; the experiment may then be repeated on a larger scale with the necessary quantity of limestone. But how much acid should be added? This again is a matter for experiment. A little (1 drop, 5 drops) is first poured down the funnel; if this causes only a slow and slight evolution of gas, a *little* more is added, and so on; when all the limestone has disappeared the addition of more acid, of course, is useless.

It should always be borne in mind that the *relative* quantities of two (or more) pure substances which take part in a chemical change are *fixed*, so that if one of them is used in disproportionate quantity (*excess*) it is wasted (unless this excess is required for some special reason).

* The 'beehive' or 'beehive shelf' (*c*) is a shallow earthenware vessel having an opening at the side through which the delivery-tube (*b*) passes, and an opening in the centre of the top through which the gas rises into the jar,

'bechive,' and the plate removed; the bubbles of gas then rise in the jar and displace the water. This is a common method of collecting a gas, which is then said to be collected *over water*, or by the *displacement of water;* a gas thus collected may contain air, and will certainly contain aqueous vapour, but as a rule this is of no consequence when the gas is required for *qualitative* experiments only.

When the first jar is filled its mouth is closed (under water) with a glass plate, and the jar is then placed on the table or left on one side in the trough, another being placed on the beehive as before. Several jars are thus filled. The rate at which the gas is evolved may be regulated by diluting the acid with water or by adding more acid as circumstances may require.

The *invisible* gas thus prepared has no distinct smell or taste,* but it produces a slightly pungent or tingling sensation when inhaled or when a stream of it plays on the tongue. When a lighted taper is put to it the gas does not take fire, and on pushing the taper down into the gas the taper is extinguished, just as quickly and completely as if it had been plunged into water. The gas, therefore, cannot be *ordinary* air; as it was once *fixed* in limestone, it was called 'fixed air' by Black (1755); it is now known as **carbon dioxide.**

It is common knowledge that some gases are lighter than air, otherwise balloons would not rise. Now carbon dioxide is *heavier* than air; when a jar of the gas is left open, mouth upwards, for a minute, the gas does not all escape, as can be shown with a lighted taper (which is extinguished); when, however, the jar is held upside-down for a minute the heavy gas falls out, and then a lighted taper placed in the jar continues to burn. This heavy gas may also be poured from one vessel to another; when a lighted candle is placed at the bottom of a large beaker and a jar of the gas is emptied into the beaker (just as if water were being poured), the candle goes out. Two large beakers may also be counterpoised on a balance and carbon dioxide poured into one of them; the air is then displaced by the heavier gas, and down goes that side of the balance. It is clear from these experiments that carbon dioxide is heavier than air, and consequently that different gases have different *densities*;* the density of carbon dioxide is 22.

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* As many gases and other substances are highly poisonous, they should only be inhaled or tasted in specified cases.

Many other beautiful experiments may be shown with carbon dioxide on a large scale; it may be poured down cardboard funnels into cardboard or glass gutters, its passage being shown by the extinction of lighted candles. A stream of it may be led to the bottom of a large glass cylinder, the gradual filling being shown by the extinction of a number of lighted candles fixed at different heights from the bottom. Soap-bubbles and balloons filled with air may be floated on the gas; petroleum, &c., burning on a plate in a shallow box may be extinguished.

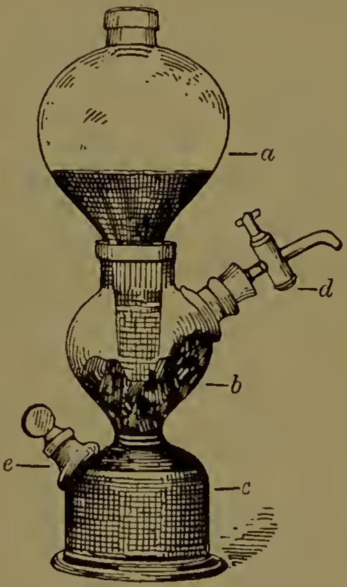

Fig. 20.

A convenient form of apparatus for the preparation of carbon dioxide and of other gases which are liberated by the action of a liquid on a solid at ordinary temperatures is shown in fig. 20 (Kipp's apparatus). The limestone, marble, or other solid is placed in the middle chamber (b). The tap (d) being open, the acid, or other liquid, is poured into the upper chamber (a) until the bottom chamber (c) is entirely and the middle chamber (b) is partly filled. The gas escapes from the tap (d). When a sufficient quantity of the gas has been obtained the tap (d) is closed, and the liquid in the chamber (b) is then forced into the lower and upper chambers by the pressure of the gas; the liberation of gas then ceases until the tap (*d*) is opened again, so that the apparatus is always ready for use. When the materials are spent the solution is emptied by removing the stopper (*e*).

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* The density (or sp. gr.) of a gas is the weight of the gas compared with that of an *equal volume* of some standard gas (hydrogen) under the same conditions (p. 160). In most cases the value is given to the *nearest whole number.*

Carbon dioxide is sold in steel cylinders (fig. 24, p. 72). The gas is forced into the cylinders under great pressure, and escapes on the valve being opened.

As carbon dioxide is so much heavier than air, it may be collected in another way. The delivery-tube (*b*, fig. 21) is passed to the bottom of a dry gas-jar; when the gas is evolved it displaces the lighter air, and by testing with a lighted taper the gradual filling of the jar can be easily followed. This method is called collecting by the *upward displacement* of air; the gas thus collected may contain air, and having been produced in contact with water, it also contains aqueous vapour.

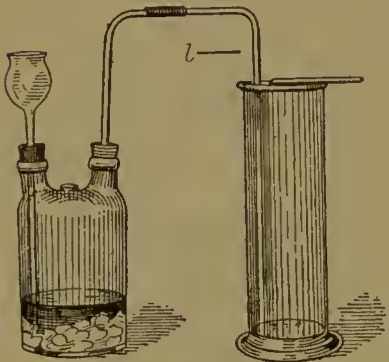

Fig. 21.

When an open cylinder which has been filled with carbon dioxide is left for some time in the pneumatic trough, it is seen that the water-level rises gradually; some of the gas has dissolved in the water. Further, if a stream of the gas is passed into a long glass tube, closed at one end, and, after a little water has been poured in, the tube is closed with the thumb and well shaken, on putting the mouth of the tube under water and removing the thumb, the water immediately rises.* A stream of the gas bubbled through some distilled water gives a *solution* of the gas, which has a rather sharp (acid) taste, which corrodes some metals, such as iron, and which changes the colour of blue litmus to a dull red; when this solution is heated the gas is expelled, and it is a general rule that the solubility of a gas *diminishes* as the temperature rises.

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* The *solubility* (or absorption co-efficient) of this and of many other gases may be expressed by stating the *volume* of the gas which is dissolved by 100 volumes of water under given conditions; at 0° the solubility of carbon dioxide is 179, at 15° only 100.

A rough examination of this (possibly impure) gas having been made, the next question to consider is whether the gas is *one* substance or a mixture; it is necessary, therefore, to ascertain whether the specific properties of the gas are fixed and constant. For this purpose the gas must first be *purified* as far as possible, because it would be useless making quantitative experiments with a substance which is certainly impure.

Now it is known that the gas contains aqueous vapour and may be mixed with air; as hydrochloric acid is volatile,* the gas may also contain this acid. How may these impurities be removed?

Hydrochloric acid (gas) is very readily soluble in water; if the carbon dioxide is bubbled through a *little* water contained in the *wash-bottle* (fig. 22), this impurity is dissolved in and retained by the water. This process is called '*washing*' the gas with water, and such a process is very often used to separate readily soluble vapours or gases from those which are less soluble.

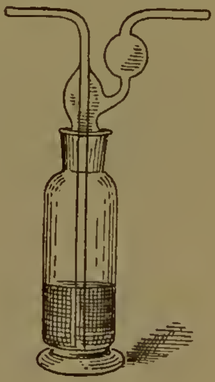
Fig. 22.

The water vapour may be removed by passing the washed gas through a porous mass of some *hygroscopic* substance (p. 38) contained in a suitable tube (drying-tube); coarsely powdered anhydrous copper sulphate (p. 38) might be used for this purpose, but several better substances are known, as, for example, anhydrous calcium chloride (p. 38), sulphuric acid (p. 39), and phosphorus pentoxide (p. 85), all of which are very hygroscopic.

The air (atmospheric) contained in the gas cannot be easily fixed and removed by using any absorbing solution or material, but if plenty of gas is allowed to flow through the whole apparatus before collecting, the sample should be free from air.

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* Hydrochloric acid is a solution of a gas (p. 143), and this gas may escape from the solution if the latter is very concentrated.

When the gas has thus been dried, obviously it would be absurd to collect it over water; it is therefore *collected over mercury*—that is to say, the jars and trough contain dry mercury instead of water—or the stream of pure gas is passed into an apparatus such as that shown (fig. 23) until all the air is expelled, and the taps are then closed.

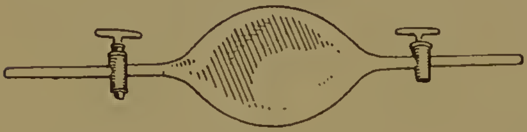

Fig. 23.

The probable or suspected impurities having been removed, is the gas now a (pure) substance or a mixture?

This question may be answered by applying the same principles as those considered in the case of solid and liquid substances—that is to say, by finding whether the specific properties (physical and chemical) of the gas are or are not constant. The solubility of different samples of the gas may be determined;* this specific property is found to be constant. The density (p. 65) may be determined. The method used will be indicated later (p. 159), and it will be shown that in weighing any gas special corrections have to be made; when this is done, it is found that under certain fixed conditions (p. 159) the weight of a litre of different samples of pure carbon dioxide is always 1·98 g., and its density 22.

Now since different samples of the purified gas from limestone have exactly the same solubility and the same density, it may be concluded that the gas is *not* a mixture; if it were, it is most unlikely that all samples would contain exactly the same proportion of the components.

Further, when different samples of the gas obtained from limestone, marble, chalk, or calc-spar, either by heating or by the action of hydrochloric acid, are examined, it is found that the samples have exactly the same solubility and the same density; this fact shows not only that the same gas (carbon dioxide) is obtained in all cases, but also that the gas is a definite substance of fixed properties. This conclusion is fully confirmed by an examination of the *chemical* properties of the gas.

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* The determination of the solubility of a gas requires special apparatus, which need not be described.

It will be shown later (p. 115) that carbon dioxide is a compound composed of two elements, carbon and oxygen.

CHAPTER X.

The Synthesis of Calcium Carbonate. Sodium Carbonate and Sodium Hydroxide.

As calc-spar is a pure substance, when it is *completely* decomposed by heat the remaining quicklime should also be a pure substance, and also the slaked lime prepared from it. This is a very important general principle which should be carefully considered.

Further experiments may now be made to see whether there is really any difference in solubility between calc-spar and slaked lime, using some quicklime prepared from calc-spar in making the slaked lime. It is thus found by special methods that there *is* a difference; the calc-spar is insoluble in water, whereas the slaked lime is slightly soluble (its solubility is 0·17 at 15°). The solution of slaked lime is called *lime-water*; a thin paste of lime-water and undissolved slaked lime is called *milk of lime*.

In determining the solubility of slaked lime by the ordinary method (p. 23) it is noticed that the clear (filtered) solution becomes milky or *turbid* while it is being evaporated, and that the residue from, say, 100 g. of saturated lime-water is no longer soluble in 100 g. of water; therefore the slaked lime *must* have changed. Further, if some lime-water be left exposed to the air for some time a crust forms at the surface; on testing this crust or deposit with hydrochloric acid, it effervesces and gives carbon dioxide. What is the explanation of this? The slaked lime in solution seems to have absorbed and combined with some carbon dioxide, which can only have come from the air.

Instead of leaving the lime-water exposed to the air, some lime-water may be poured into a gas-jar containing carbon dioxide; on shaking, a solid is *precipitated*, causing the liquid to look 'milky.' In order to prepare a larger quantity of this solid, a stream of (washed) carbon dioxide may be slowly bubbled through a large volume of lime-water for a few moments;* the precipitate is then separated by filtration, washed, dried at 100°, and examined. It is found to have the following properties: it is insoluble in water; it is decomposed when heated, giving carbon dioxide and quicklime; it gives carbon dioxide when treated with hydrochloric acid; it is constant in composition, and every sample thus prepared loses 44 per cent. of gas and gives 56 per cent. of quicklime. This precipitate, therefore, is identical with calc-spar in composition; it must be the same compound as calc-spar; the only difference between it and calc-spar, no matter what test is applied, is a difference in the *size* of the crystals; if calc-spar be ground to a fine powder, even this slight and chemically unimportant difference (p. 28) vanishes.

The compound which occurs in nature in a pure state as the mineral calc-spar, and which can also be produced from slaked lime and carbon dioxide as shown above, is called **calcium carbonate.**

Since calcium carbonate is composed of quicklime and carbon dioxide, how can it be formed from slaked lime and carbon dioxide when quicklime and slaked lime are not identical? In order to clear up this difficulty the relation between slaked lime and quicklime must be considered. Slaked lime is formed when water is added to quicklime; it seems, therefore, that quicklime combines with water. Quantitative experiments confirm this conclusion.

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* The precipitate may disappear if the gas is passed for some time, because it is then changed into a soluble substance (p. 272).

When a weighed quantity of quicklime is 'slaked' with plenty of water, and the *wet* slaked lime is then dried at 100°, *some* of the added water passes away as steam, but a *fixed* quantity remains in the slaked lime after heating at 100° until the residue is *constant* in weight (p. 23). 56 g. of quicklime always give 74 g. of slaked lime.

The water which thus remains cannot be *moisture* (p. 37); it cannot be merely mixed with the quicklime as liquid water. Slaked lime, therefore, is quicklime which has *combined* with water to form a compound, known as **calcium hydroxide,** which differs altogether in properties from either of its constituents.* When calcium hydroxide (74 g.) is very strongly heated (at about 530°) it decomposes, giving quicklime (56 g.) and water (18 g.).

Now since slaked lime (calcium hydroxide) and carbon dioxide form calcium carbonate (a compound of quicklime and carbon dioxide only), it must be concluded that when calcium hydroxide is treated with carbon dioxide, *water* is formed, as well as calcium carbonate. That this is so may be shown by passing *dry* carbon dioxide over *dry* slaked lime which is heated at 100°.

For this experiment some calcium hydroxide, dried at 100° (until constant), is placed between plugs of dry cotton-wool in the inner tube (*a*) of a Liebig's condenser (fig. 24), and heated at 100° by passing steam from (*b*) through the outer jacket. A slow stream of carbon dioxide (from the steel cylinder, *c*) is then passed through the slaked lime, the gas having been first led through the drying-tube (*d*), which contains anhydrous calcium chloride (p. 38). After some time a liquid which can be identified as *water* collects in the cold receiver (*e*), and if the solid in the inner tube is afterwards examined, it can be identified as calcium carbonate.

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* Although calcium hydroxide is formed from quicklime and water, it does not contain water *as such;* that is to say, there is no *liquid* in it, just as there is no *gaseous* carbon dioxide in calcium carbonate, no gaseous oxygen in copper oxide. The matter of which water consists is completely changed in properties when it enters into chemical combination. The water formed by decomposing calcium hydroxide is *not* regarded as water of crystallisation or hydration (p. 37) for reasons which will be discussed later.

If a *weighed* tube containing anhydrous calcium chloride is attached to the outlet of the tube (*a*) and all the water produced is driven into it, the experiment may be made quantitatively, using, of course, a weighed quantity of slaked lime and *excess* of dry carbon dioxide; it is then found that 74 g. of slaked lime (and 44 g. of carbon dioxide) give 100 g. of calcium carbonate and 18 g. of water.

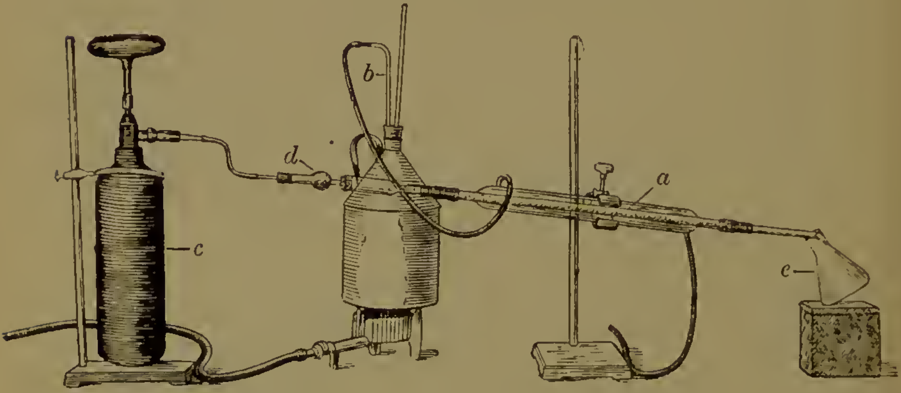

Fig. 24.

As calcium carbonate is a compound of quicklime and carbon dioxide, is it possible to produce this compound from its two constituents? When some *dry* carbon dioxide is confined over mercury in a tube, and some pieces of *dry* quicklime are pushed under the open end of the tube, although the quicklime rises and comes into contact with the gas the volume of the latter does not diminish appreciably even in the course of some hours. Hence combination does not occur at *ordinary* temperatures.

The fact that calcium carbonate is a compound has now been proved in two different ways: firstly, by decomposing it into two different substances; secondly, by forming it (together with water) from two different substances.

The first of these methods, the breaking up of a compound into different substances (elements or simpler compounds), is termed *analysis;* the second method, the production of a compound from its constituents (elements or simpler compounds), is called *synthesis.*

The results of such analytical and synthetical quantitative experiments with calcium carbonate and calcium hydroxide may be summarised as follows:

Calcium carbonate gives Quicklime and Carbon dioxide.
100 g. 56 g. 44 g.

Quicklime and Water give Calcium hydroxide.
56 g. 18 g. 74 g.

Calcium hydroxide + Carbon dioxide = Calcium carbonate + Water.
74 g. 44 g. 100 g. 18 g.

Since all these compounds are fixed and definite in composition, and the figures given above express their quantitative relationships, it is a simple matter to calculate the weight of, say, quicklime, which would be obtained from any given quantity of pure calcium carbonate or slaked lime. Examples need hardly be given.

All the changes summarised above are further illustrations of chemical change—decomposition or combination; they also afford further evidence of the indestructibility of matter, and of the constant and fixed composition of compounds.

It has been stated, but without giving experimental evidence, that carbon dioxide is a compound of carbon and oxygen; quicklime is also a compound of two elements, calcium and oxygen, and is called **calcium oxide.** These two compounds will be referred to later. Calcium carbonate, therefore, is itself a compound of three elements, calcium, carbon, and oxygen.

Returning once more to limestone, marble, and chalk, it has been stated that when these materials are heated they all give carbon dioxide, but the loss in weight is not constant, and varies from about 43 to 44 per cent.

The residue in all cases behaves like pure quicklime (p. 69), and slakes with water; *but* when the slaked lime from, say, limestone is treated with water it does not dissolve *completely*, even when far more water is added than is known to be required for the solution of an equal weight of *pure* slaked lime. A part of the material, perhaps only about 0·5 per cent., is *insoluble* in water, and can be separated by filtration; this part *cannot* be slaked lime; the limestone, therefore, contained some impurity, something which is not calcium carbonate. The same conclusion is arrived at by testing limestone with hydrochloric acid; as a rule, the limestone does not disappear entirely, but a small quantity of some insoluble residue, which, therefore, *cannot* be calcium carbonate, remains. Similar results are observed when marble and chalk are examined by these methods, *but* the percentage of impurity is generally smaller than in limestone.

Here, then, is the explanation of the fact that these materials are not absolutely constant in composition; they are all *impure* calcium carbonate, and the percentage of impurity varies. By converting into quicklime, treating with water, and then bubbling carbon dioxide through the filtered solution of the calcium hydroxide, a pure substance of fixed composition, namely, calcium carbonate, is obtained; by this treatment the impurities in the limestone, marble, or chalk are removed, and the pure compound is isolated by chemical methods.

Calcium carbonate is a component of several naturally occurring materials in addition to those already mentioned. *Coral*, which occurs in enormous quantities, forming coral-reefs, in some tropical seas, and which is the 'skeleton' of the coral polyp, consists principally of calcium carbonate, as do also those beautiful mineral formations known as stalactites and stalagmites (p. 273). Pearls, egg-shells, and the shells of many aquatic animals also contain a large proportion of calcium carbonate. *Aragonite*, a transparent mineral, found in small quantities, is pure calcium carbonate; it differs from calc-spar in crystalline form, specific gravity, and some other physical properties.*

Dolomite, a material which forms vast mountain-ranges ('the Dolomites' of the Tyrol, &c.), consists principally of a mixture of calcium carbonate and a very similar compound known as *magnesium carbonate.*

The case of calcium carbonate may indicate the manner in which natural materials are examined and classified chemically—how it is proved that several apparently different minerals consist almost entirely of one definite substance.

SODIUM CARBONATE AND SODIUM HYDROXIDE.

From very early times the cleansing properties of the ashes of plants have been known and utilised, and several substances which had this and other properties in common came to be classed together as **alkalis** (alkali, *the ash*). These alkalis were found to change the colour of certain vegetable dyes, and also to have a burning or *caustic* action on animal and vegetable matter. Quicklime (or slaked lime) which was very vigorous in its action was called a *caustic alkali*, whereas sodium carbonate (p. 35) and potashes (a material obtained from the ashes of land plants, p. 276) were termed *mild alkalis;* the latter effervesced when placed in acids, and in this respect behaved like limestone (calcium carbonate), so that this substance was also regarded as a mild alkali; it was also known that when quicklime was added to a solution of a mild alkali, such as potashes, the latter became caustic and no longer effervesced with an acid.

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* This statement that *pure* calcium carbonate exists in two forms (calc-spar and aragonite) which *differ* in physical properties seems to contradict what has already been said as to the specific properties of a substance being constant. But just as changing to ice at 0° is a specific property of water, so the possibility of crystallising in one of two forms is a specific property of calcium carbonate. The crystals of calc-spar and of aragonite are composed of identical particles of matter, but the *arrangement* of those particles is different in the two cases; this difference in arrangement causes differences in specific gravity (and other properties) of the crystals as a whole.

Before 1755 it was supposed that the mild alkali, limestone, became the caustic alkali, quicklime, by absorbing 'fire-stuff' in the process of burning; but in that year Black proved that the change was due to the *loss* of some gas ('fixed air,' p. 64). He also showed that this gas was contained in other mild alkalis, and could be transferred from them to quicklime (calcium oxide), the mild alkali becoming caustic, the quicklime being converted into calcium carbonate.

This change may now be studied; but instead of using quicklime a clear solution of calcium hydroxide may be employed, as the 'reaction' is then more easily observed. On mixing clear solutions of lime-water and sodium carbonate a slight precipitate is produced;* when this is separated by filtration, washed, and dried, it is found to be identical with calcium carbonate. The matter of which carbon dioxide is formed must have been taken from the sodium carbonate by the calcium hydroxide. What else has been formed?

In order to answer this question the *filtrate* from the calcium carbonate must be examined; but it is obvious that it would be useless to simply mix indefinite quantities of lime-water and sodium carbonate together, because since quicklime (or calcium hydroxide) combines with a *fixed* weight of carbon dioxide, unless the substances are used in the required proportion, the filtrate must contain either unchanged calcium hydroxide or unchanged sodium carbonate, in addition to any new substance which may have been formed. What quantities, then, shall be taken?

It is known that 74 g. of calcium hydroxide combine with 44 g. of carbon dioxide, giving 100 g. of calcium carbonate and 18 g. of water, so that if the percentage of carbon dioxide in sodium carbonate were also known it would be possible to calculate the required proportion of slaked lime and sodium carbonate, assuming that all the carbon dioxide in the sodium carbonate passes to the quicklime.

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* As the solubility of calcium hydroxide is very small (p. 69), only a small quantity of precipitate can be produced unless a very large volume of lime-water is used.

Now when *hydrated* sodium carbonate is gently heated it loses all its water of hydration (p. 38), but it does not decompose and give off carbon dioxide as does calcium carbonate; hence the quantity of carbon dioxide contained in the (*anhydrous*) crystals must be estimated in a different manner from that used in the case of calcium carbonate.

For this purpose a weighed quantity (say 2 g.) is placed in a flask (fig. 25) fitted with a calcium chloride tube (*a*), and containing some water and a small tube (*b*) partly filled with diluted hydrochloric acid. The whole apparatus is first weighed, and then by tilting it carefully a little of the acid is caused to flow into the sodium carbonate solution; the liberated carbon dioxide passes through the calcium chloride tube (it cannot pass through the tube *c*), and the *dried* gas escapes. When the effervescence has subsided the apparatus is again tilted carefully, and this process is repeated until all the sodium carbonate has been changed. *Dry* air is then passed through the tube (*c*) to displace all the heavy carbon dioxide, and the apparatus is weighed again. The loss in weight gives the weight of the carbon dioxide which is obtained from the given weight of sodium carbonate.

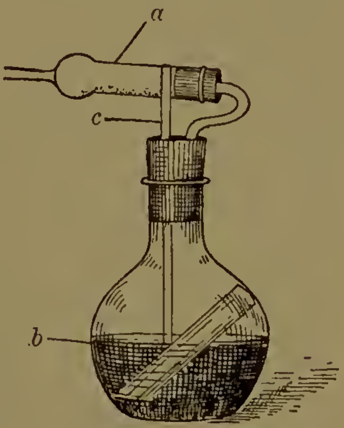

Fig. 25.

Accurate experiments show that 106 g. of anhydrous sodium carbonate must be used to supply 44 g. of carbon dioxide, which is the quantity required to convert 74 g. of calcium hydroxide into calcium carbonate (p. 73).

Dry slaked lime and anhydrous sodium carbonate in the proportion of 74 to 106 parts by weight (say 7·4 to 10·6 g.) are now placed together in a flask with some water (say 250 c.c.), and after being warmed gently for some time * the solution is filtered from the calcium carbonate which has been formed. If the experiment has been done accurately, the filtrate gives no effervescence on testing a portion with hydrochloric acid, and no precipitate on testing another portion with a solution of sodium carbonate; these tests prove that the filtrate contains neither sodium carbonate nor calcium hydroxide.

When such a filtrate is evaporated on a water-bath it gives a syrup, which does not yield a solid residue until after it has been strongly heated † in a silver or iron basin and then cooled; this solid is the caustic alkali, and is now called *sodium hydroxide* (or caustic soda).

Sodium hydroxide is deliquescent (p. 38) and very readily soluble in water, its solution having a soapy feel; it is a very violent or active substance, and burns the skin and decomposes nearly all animal and vegetable matter; it even attacks glass and earthenware at high temperatures, hence the use of a silver basin. Soaps are made by boiling vegetable oils with sodium hydroxide (p. 279).

When a solution of sodium hydroxide is passed up into a tube containing carbon dioxide confined over mercury, the gas is rapidly and completely absorbed, provided that it is pure and enough sodium hydroxide is used; the gas is not expelled again when the solution is boiled, as it is from its aqueous solution, because it has combined with the sodium hydroxide, giving sodium carbonate and water, just as it combines with calcium hydroxide, forming calcium carbonate and water (p. 72). A mixture of sodium hydroxide and calcium hydroxide which has been strongly heated to dry it thoroughly is very porous, and is often used to absorb carbon dioxide; such a mixture is known as *soda-lime.*

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* As no *visible* result occurs, and it is impossible to see when the change is complete, it is advisable to leave the two substances together for some time, and to hasten the reaction by warming; the filtrate is then tested as described above.

† Great care should be taken that the solution does not spirt into the face while it is thus being heated.

When a solution of sodium hydroxide or calcium hydroxide is added in sufficient quantity to some litmus which has been reddened by an acid, the colour again changes to blue; that is to say, the effect of the acid on the dye is 'neutralised.'*

Several compounds similar to sodium hydroxide and calcium hydroxide in chemical properties are known; as, for example, **potassium hydroxide** (caustic potash), a compound which may be obtained from potashes (potassium carbonate), just as sodium hydroxide is obtained from sodium carbonate. The term *alkali* is now restricted to substances of this type (p. 253).

CHAPTER XI.

Oxygen.

When copper is heated in the air a black substance, copper oxide, is formed (p. 46); the weight of this product is greater than that of the copper from which it is obtained, because the metal combines with some matter from the air.

Now many metals behave like copper in this, that when heated in the air they slowly change, lose their metallic appearance, and give 'earthy' products, the weights of which are greater than those of the metals from which they are produced.

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* Calcium carbonate does not change the colour of a wet red-litmus paper (p. 40), but calcium hydroxide turns it blue; the two compounds may thus be easily distinguished by this test. Although sodium carbonate belongs to the same class or type of compound as calcium carbonate (they are both 'salts,' p. 253), it has an action on red-litmus solution similar to that of calcium hydroxide; calcium carbonate, being insoluble, does not act on litmus.

Two substances obtained in this way from lead have been known from early times. When lead is heated (in an open iron ladle) it first melts—that is to say, changes in state—and then a gray or coloured scum or dross appears at the surface; the metal tarnishes and gives a 'calx.' If this dross is removed with a rag and the bright metal is kept melted the dross comes again, and the longer the lead is heated the more dross is formed, until finally, in place of the melted metal, a yellowish or reddish-brown solid called *litharge* (or *massicot*) is obtained.

When the lead is melted in a tube from which the air is practically excluded (compare copper, p. 41) no appreciable quantity of litharge is produced, from which it may be concluded that when the change occurs in the air, the metal combines with some matter from the air, and that litharge is a compound.

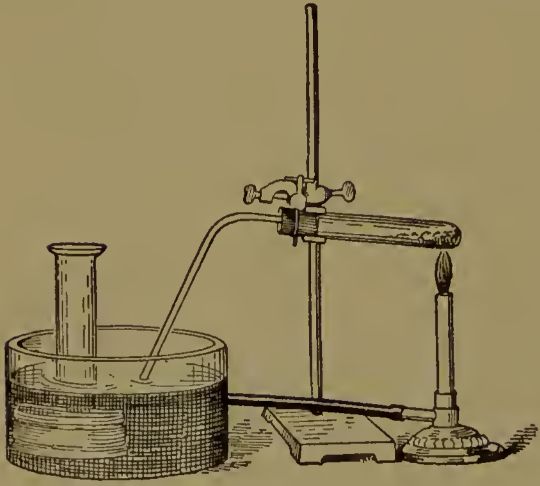

Fig. 26.

Although litharge does not change when it is heated strongly (say at 500°) in the air, it does so in a remarkable manner when it is heated *gently* (at about 300°), and is slowly transformed into a scarlet powder known as *red-lead*.

This change can be brought about by spreading a thin layer of powdered litharge over an iron plate and then heating underneath with a Bunsen-flame; in some places the litharge is raised to a suitable temperature and red-lead is formed.

Since red-lead is manufactured by heating litharge in the air, it hardly seems likely that red-lead would change if it were heated alone, but as a matter of fact it does so very quickly. When heated in an angle-tube (fig. 26) it first becomes much darker in colour,* and for a few moments bubbles of air escape from the delivery-tube; after a short interval bubbles again escape from the tube, and when these are collected over water (p. 64) it is seen that the volume of the gas obtained is far greater than that of the air originally contained in the tube; therefore this air or gas must have come from the red-lead. When no more gas is evolved the delivery-tube is withdrawn from the water and the tube is allowed to cool (it will probably crack); in the place of the red-lead there is now a yellow substance (litharge).†

This experiment shows that red-lead is a *compound*, which can be decomposed into a yellow solid and an invisible gas; red-lead could hardly be a *mixture* of these. As the gas must have been taken up by the lead from the air it might be inferred that the gas was air, especially as it has no smell. When, however, a glowing wooden chip is pushed down into the gas, the wood bursts into flame. This simple test shows that the gas is not ordinary air.

Another scarlet powder, similar to red-lead in appearance, but obtained by heating the metal mercury (quicksilver) in the air, is known; this substance is called *mercuric oxide*. When it is heated in a tube similar to that just used (fig. 26), its colour first changes to a dark brown;* after some time a gas is evolved and may be collected over water; small drops of shining liquid are condensed on the colder portions of the tube. When heated long enough the powder disappears completely; it has all been *decomposed* into an invisible gas and the liquid metal mercury. The gas thus obtained, like that prepared from red-lead, causes a glowing chip to burst into flame.

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* This first change in colour is possibly due merely to a change in the crystalline form of the substance, and may be regarded as a physical change which precedes decomposition.

† The colour of litharge depends to a great extent on whether it has been cooled quickly or slowly, and commercial litharge is often of a reddish-brown colour because it contains some red-lead.

The decomposition of red-lead and of mercuric oxide was studied by Priestley in 1774; he concluded that the gas obtained was some purer kind of air than ordinary air, and he named it 'dephlogisticated air' (p. 129). Just before this time Scheele, by strongly heating mercuric oxide, nitre, and some other substances, had also prepared this gas, which he called 'fire air.' About thirty years later Berthollet found that this gas could be obtained by heating *potassium chlorate;* this colourless crystalline substance is now generally used for the preparation of the gas on a laboratory scale.

The potassium chlorate (compare footnote †, p. 62) is heated in an angle-tube (fig. 26). After some time it melts (at 351°), and later on begins to effervesce owing to the escape of a gas, which is collected over water. The melted substance in the angle-tube becomes thicker as the heating is continued, and may even solidify, although its temperature has not been lowered. After some time the evolution of gas slackens and finally ceases; the delivery-tube is then immediately taken out of the trough, so that water does not run into the apparatus when the flame is removed. The melted substance in the angle-tube solidifies on cooling to a crystalline mass, which obviously cannot be potassium chlorate, as it does not give any gas when it is heated; if this solid is crystallised from water, and its crystals are compared with those of potassium chlorate obtained in a similar way, a noticeable difference will be seen in the geometrical form. The solubility of this solid is also very much greater than that of potassium chlorate, as can be shown even by rough quantitative experiments, and its melting-point is very much higher (about 750°). In fact, the two substances are different in specific properties. The solid thus obtained by decomposing potassium chlorate is called *potassium chloride;* it is easily distinguished from potassium chlorate by a chemical test described later (p. 150).

In preparing a considerable quantity of this gas for laboratory or lecture experiments, powdered potassium chlorate is mixed with about 2 per cent. of pure manganese dioxide.* When this mixture is *gently* heated in a flask (or angle-tube) the gas is evolved rapidly, and at a temperature below that required to decompose potassium chlorate even very slowly, but the volume of the gas thus obtained is the *same* as that which would have been produced if the potassium chlorate alone had been used. The manganese dioxide is *unchanged* at the end of the process. This can be proved by separating it from the potassium chloride in the residue (manganese dioxide is insoluble in water), and then washing, drying, and examining it; also by making quantitative experiments, which show that the weight of the *recovered* manganese dioxide is the same as that of the substance originally added to the potassium chlorate (compare p. 233).

The gas obtained by *any* of the methods given above has no smell, and produces no noticeable effect when it is inhaled. While being collected it does not *seem* to dissolve in water, but careful observations show that it is in fact slightly soluble. The gas does not take fire when a light is put to it, but when a lighted candle is let down into the gas, burning or combustion goes on much more rapidly than in the air. A piece of charcoal, heated on a deflagrating-spoon (fig. 27)† in

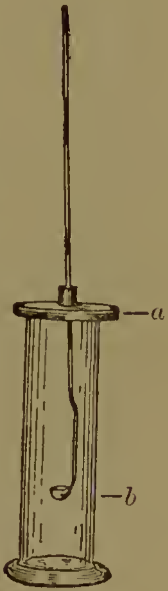

Fig. 27.

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[*] A small quantity of the mixture is first prepared and tested by heating it in a test-tube, because if the manganese dioxide contains charcoal (as it sometimes does) a violent explosion may occur.

[†] A bent iron wire, fitted with an adjustable brass disc (*a*, fig. 27), and at the bottom with a small copper cup (*b*). It is placed in the jar of gas as shown.

the Bunsen-flame, merely glows; when, however, it is then plunged into a jar of the gas it burns brilliantly. Sulphur (p. 211), which burns languidly in the air, also burns far more rapidly in this gas, with a beautiful blue flame; during or after this experiment a disagreeable suffocating smell is noticed in the neighbourhood of the jar.

A small piece (0·5 g.) of phosphorus,* when ignited on a deflagrating-spoon, burns vigorously in the air, emitting a dense white smoke, but when plunged into a jar of the gas it burns much more fiercely. The smoke is caused by particles of a white solid substance, which gradually settle on the bottom and sides of the vessel.

A ribbon of the metal magnesium burns in the air when it is heated in a Bunsen-flame, and with even greater brilliancy when it is placed in a jar of the gas, a colourless solid substance being formed.

A ribbon of steel or iron, such as a watch-spring, does not 'burn' in the air; when, however, such a ribbon is tipped with a little burning sulphur and plunged into a jar of the gas, the iron begins to burn brilliantly, and red-hot drops fall to the bottom of the cylinder (which is covered with a layer of sand to prevent the glass from being cracked), where they solidify to hard black lumps.

The chemical changes which take place during some of these burnings or combustions are considered later; in the meantime it may be pointed out that although a part or the whole of some of the materials (wax, charcoal, sulphur) disappears entirely, the matter of which the material is composed is not destroyed, but is changed into matter which is invisible.

When samples of the gas prepared by heating red-lead, mercuric oxide, nitre, and potassium chlorate respectively are examined qualitatively in the manner indicated by the above experiments, they are found to have the *same* properties; that is to say, they are all invisible, odourless, and non-inflammable, and a given substance burnt in any of these samples yields one and the same result. Further, when samples of the gas obtained from the given compounds are washed with water (or otherwise purified if necessary) and dried (p. 67), and are then examined quantitatively, they are found to be identical. For example, they have all the same *solubility*[*] (4·86 at 0°, 3·36 at 15°); a litre of every sample, measured under special conditions, weighs 1·43 g., and the density of the gas is 16 (p. 65); all the samples give rise to copper oxide when they are passed over heated copper. The same gas, therefore, is obtained from red-lead, mercuric oxide, nitre, and potassium chlorate; this gas is fixed and constant in properties, therefore it is a (pure) substance and not a mixture. The name **oxygen** was given to this gas by Lavoisier (p. 248).

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* Phosphorus must not be touched with the fingers, as the warmth of the hand may cause it to take fire; it is held with tongs, cut under water, and dried with filter-paper.

Oxygen, like copper, has never been decomposed; matter may be added to it, combined with it, but except in this way it has never yet been changed; it is an *element*.

Oxygen is a very important and abundant element, and about one-half of the total matter of the earth, including the ocean, consists of combined oxygen; it unites with nearly all the other elements, forming compounds which are called *oxides;* thus copper oxide and mercuric oxide are compounds of oxygen with the elements copper and mercury respectively. The white solid which is formed from phosphorus and oxygen is known as *phosphorus pentoxide;* it is extremely hygroscopic, and deliquesces (p. 38) on exposure to moist air; as it absorbs water vapour so readily it is very often used in drying air and other gases (p. 67). The suffocating invisible gas formed from sulphur and oxygen is called *sulphur dioxide* (p. 229), and the metals magnesium and iron combine with oxygen to form *magnesium oxide* and *iron oxide* respectively. With many elements oxygen forms two or more different compounds; thus litharge and red-lead are both *oxides* of lead, but red-lead contains a larger proportion of oxygen than does litharge.

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[*] Compare p. 66.

Since red-lead is *decomposed* into litharge and oxygen, and is *formed* by the combination of litharge and oxygen at lower temperatures, it is clear that some chemical changes are *reversible*, just as are changes in state. As a further example of a reversible chemical change, the case of quicklime and water $\longleftrightarrow$ calcium hydroxide (p. 71) may be mentioned. It is, however, rather the exception than the rule for a chemical change to be reversible under attainable conditions; the oxides of magnesium and iron, for example, are not decomposed into metal and oxygen at the highest temperatures yet reached. Oxides, as a class, are not decomposed when they are heated; the behaviour of mercuric oxide in this respect must be regarded as rather exceptional.

The conversion of an element into its oxide is often termed *oxidation*, and the element which has undergone the change is said to be *oxidised*.

CHAPTER XII.

The Atmosphere.

The gaseous matter which surrounds the earth, in which we live and move, which itself moves, causing wind, is known as the 'air' or atmosphere. Now it has already been noted (p. 17) that this matter has weight; that the atmospheric pressure, or weight of the atmosphere at sea-level, is, on the average, equal to that of a column of mercury 760 mm. high. It has also been noted that the air contains aqueous vapour, from which clouds, mist, dew, rain, hail, or snow may be formed when the temperature falls. Further, it has been stated (p. 70) that when lime-water is exposed to the air the calcium hydroxide in solution is slowly changed and precipitated as calcium carbonate, a fact which proves that the air contains carbon dioxide. From the experiments with metals (p. 79) it is also clear that the air contains the element oxygen.

Now when some powdered anhydrous calcium chloride (p. 38), say about 20 g., is placed on a clock-glass and counterpoised on the pan of a balance, it is found that it rapidly gains in weight and becomes damp, because it absorbs and fixes water vapour from the air circulating above it. The damp powder may be heated and the water which is given off may be collected and identified (p. 14). If, however, a glass cylinder full of ordinary air is inverted over some of the dry, hygroscopic powder, contained on a watch-glass floating on mercury, the volume of the air in the cylinder does not diminish very appreciably even after several hours; this fact proves that when the water vapour is abstracted from the air there is very little diminution in volume.

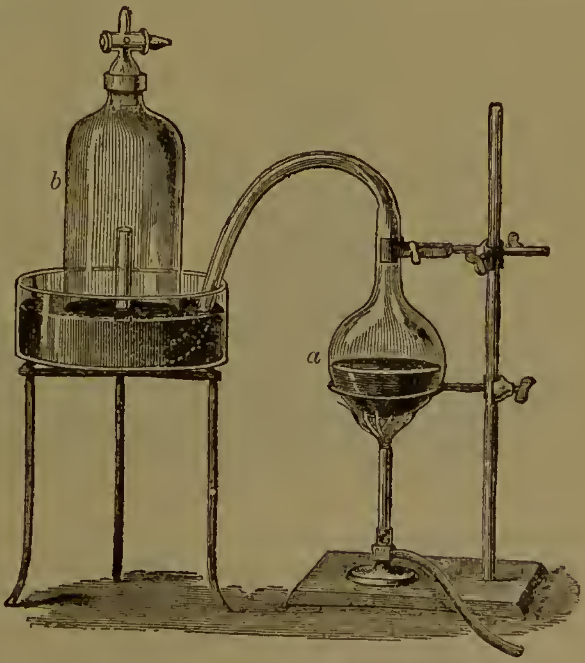

Fig. 28.

Now the carbon dioxide and aqueous vapour contained in a confined volume of air may be abstracted by leaving the air exposed to soda-lime or sodium hydroxide (pp. 78, 79) in a similar manner; here again there is only a small change in volume, and the gas which remains is certainly not merely oxygen, as a glowing chip plunged into it is not kindled into flame.

What else, then, does the air contain?

When Priestley discovered oxygen in 1774, he described his experiments to Lavoisier, who repeated them in the following manner:

A retort (*a*, fig. 28) containing mercury and air was placed as shown, with its open end turned upwards in a trough containing mercury and covered with a large bell-jar (*b*); the air in the retort and bell-jar was thus shut off from the outside atmosphere. The mercury in the retort was then heated at about 300° during several days; some of the mercury changed, giving the scarlet powder, mercuric oxide, and the volume of the air *diminished*, as shown by the mercury rising in the bell-jar (*b*); after some days no further change occurred, no more mercuric oxide seemed to be formed (although a lot

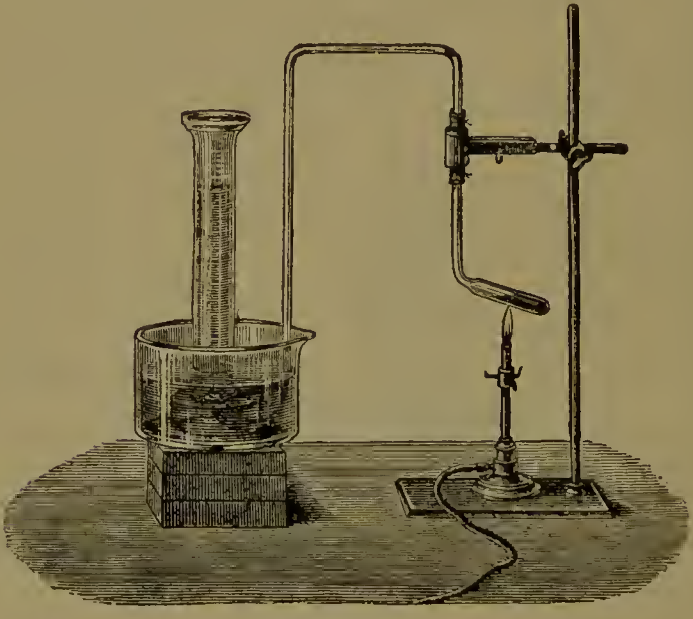

Fig. 29.

of mercury remained in the retort), and the level of the mercury in (*b*) remained stationary. After the whole apparatus had been allowed to cool, it was found that *about* one-fifth of the air had disappeared, and a lighted candle plunged into the gas which was left was at once *extinguished.*

The mercuric oxide which had been formed was collected and strongly heated in the tube (fig. 29); the evolved gas, which was collected over mercury, was found to kindle a glowing chip or piece of charcoal, and its volume was found to be about the same as that of the 'air' which had been absorbed.

These experiments showed that mercury combines with and fixes oxygen (undergoes oxidation) when it is heated in the air, but that only a portion of the air, namely, about 20 per cent. by volume, is thus fixed by mercury. The remaining 80 per cent. (by volume) cannot be oxygen, because it is *not* fixed by mercury, and because a candle does not burn in it.

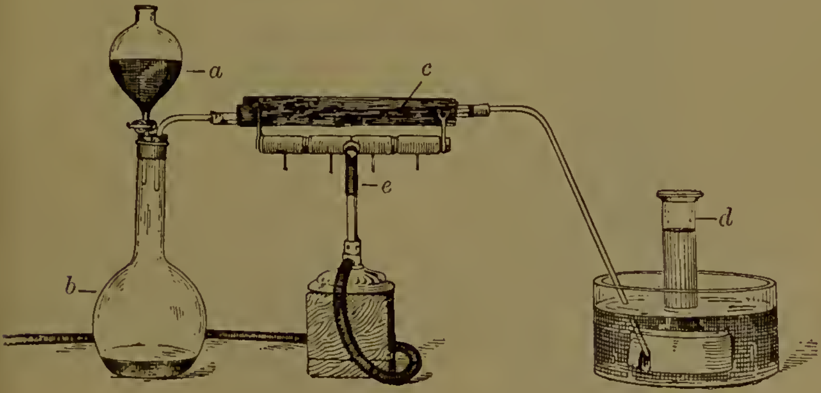

Fig. 30.

Now, as already stated, there are many metals besides mercury which combine with the oxygen in the air. Of such, copper and iron may be conveniently employed to absorb and fix atmospheric oxygen. By dropping water from the tap-funnel (*a*, fig. 30), air from the flask (*b*) is slowly passed over a long roll of copper gauze, contained in the glass tube (*c*) and heated by the burner (*e*); the copper near the inlet is slowly converted into black copper oxide, and although the 'air' then passes over plenty of hot unchanged copper, it is not entirely absorbed or fixed, but a large proportion escapes from the outlet-tube and may be collected over water. This gas (*d*) is found to be different from ordinary air, since a lighted candle placed in it is immediately extinguished; only about one-fifth of the air by volume is absorbed by the copper.

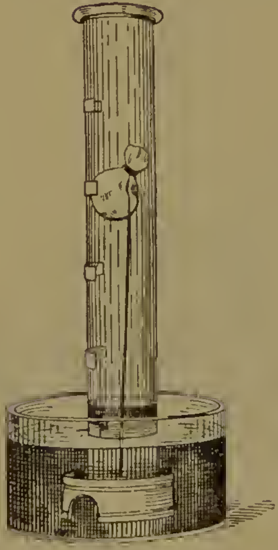
Fig. 31.

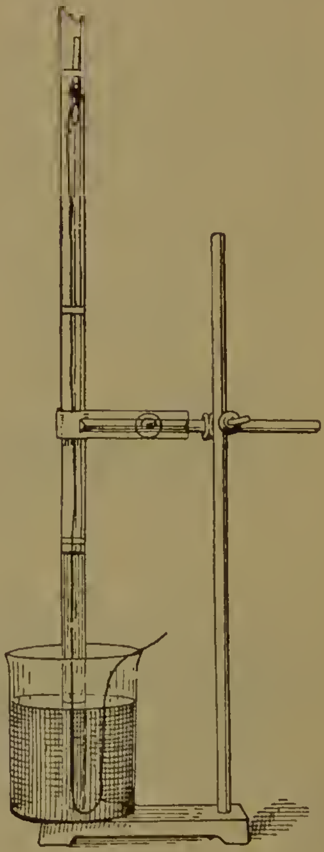
Fig. 32.

When some iron filings or borings are moistened with water and placed in a muslin bag, which is then suspended with the aid of a bent wire in a cylinder full of air, inverted over water (fig. 31), the water slowly rises in the jar, but after some days its level remains constant, about one-fifth of the air having been absorbed. When the bag is withdrawn and the jar is placed mouth upwards on the table, a lighted candle placed in the gas is immediately extinguished. On examining the iron it is found to have rusted, from which fact it might be inferred that rust is an oxide of iron.

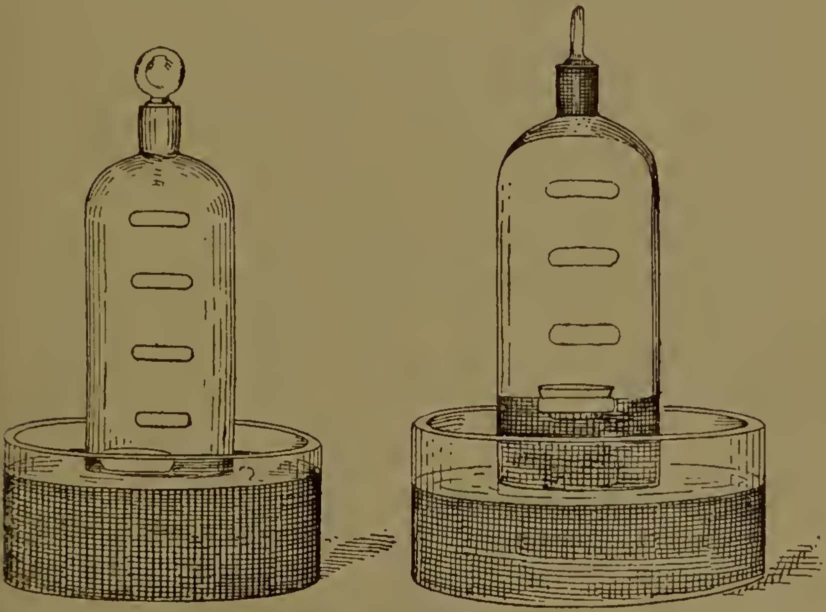

Fig. 33.

When a stick of phosphōrus,* supported by copper wire, is placed in a long glass tube, sealed at one end and inverted over water (fig. 32), the level of the water slowly rises and about one-fifth of the air is absorbed; the remaining gas extinguishes a lighted taper. In this experiment although the phosphorus fumes a little it does not *seem* to change, and yet some of it must have done so, because if phosphorus is not present the volume of the air does not diminish appreciably.*

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* Compare footnote, p. 84.

If a dry piece of phosphorus (2 to 3 g.) is placed in a porcelain dish floating on water, and then covered with a large, narrow, dry bell-jar (fig. 33), it can be made to burn in the confined volume of air. For this purpose the stopper of the jar is removed, and after waiting until the levels of the water inside and outside are the same, the phosphorus is ignited † and the stopper quickly and securely replaced. The heat generated by the burning or combustion of the phosphorus causes the enclosed air to expand—it may be necessary to hold the bell-jar—and at first the water-level in the bell-jar is depressed; as burning progresses, however, the water begins to rise again, and when the flame has died out completely and the apparatus has cooled to its initial temperature, the volume of the gas in the jar is seen to be less by about one-fifth than the original volume of the air. If now some water is run into the trough until its level is the same as in the jar, air will not enter the bell-jar on the stopper being removed, and it can be shown that the gas which is contained in the jar extinguishes a lighted candle.

During the burning of the phosphorus a white solid is formed, some of which settles on the bell-jar; this product is the same as that obtained when phosphorus burns in oxygen, and being extremely hygroscopic, it soon *deliquesces* (p. 38).

All these experiments show that when certain substances are heated in, or left in, the air, part of the air disappears, and there remains a gas which is *not* absorbed by these substances and which extinguishes flame. Although the experiments are only rough ones, it is found that practically the same proportion of the air—viz. one-fifth—disappears or is absorbed in every case;* it may be concluded, therefore, that one and the same gas is taken up by mercury, copper, iron, and phosphorus, viz. the gas oxygen, and that consequently the unabsorbed gas or residue is *the same* in all these experiments.

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* There are two reasons why no *obvious* change occurs: firstly, only a very small proportion of the phosphorus is acted on; secondly, the product is deliquescent and dissolves.

† By touching it with a hot wire.

Until quite recently (1900) this residue or unabsorbed gas, which is colourless and odourless and in which burning substances are extinguished, was regarded as *one* (pure) substance; it is now known, however, that although it consists almost entirely of one element, **nitrogen**, it contains a number of other elements (*Helium*, *Neon*, *Argon*, *Krypton*, *Xenon*) in relatively very small quantities.

By experiments such as the above it can be shown that various gases as well as aqueous vapour are contained in the atmosphere, and a rough idea of their relative proportions by volume may be obtained.

Accurate analyses of mixtures of gases are only possible with the aid of special apparatus, and the direct observations are of little value until they have been corrected according to principles explained later (p. 152); for these reasons it is only possible to indicate here some of the simpler methods used in the analysis of air.

The *aspirator* (*a*, fig. 34) filled with water is connected to a tube (*b*) filled with anhydrous calcium chloride, a tube (*c*) filled with soda-lime, and a tube (*d*) filled with anhydrous calcium chloride; the tubes (*c*) and (*d*) are weighed. A known volume of air is then slowly drawn through these three tubes by opening the screw clamp (*e*) and measuring the volume of water which siphons out of the aspirator (filling it as often as is necessary). The aqueous vapour is absorbed in (*d*), the carbon dioxide in (*c*), and the *weights* of these substances in the measured *volume* of air are ascertained by weighing again at the end of the experiment. (What is the use of the tube (*b*)?)

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* In the experiments with iron and phosphorus (figs. 31–33) the volume of the air contained in the vessels at the commencement of the experiment may be previously measured with the aid of water and a graduated cylinder; this volume is then divided into five equal parts (as shown in the diagrams), the divisions being marked on the vessel with labels covered with wax.

As the weight of a litre of water vapour (p. 161) and that of a litre of carbon dioxide (p. 68) are known, the *volumes* of these substances which have been absorbed may be calculated.

The *weight* of oxygen in a known volume of dry air may be determined by passing the air over heated copper and finding the increase in weight; as the density of oxygen is known (p. 85), its *volume* may then be calculated. The *volume* of oxygen in a given volume of air may also be determined by absorbing the gas with moist phosphorus in the manner already described. The volume of the nitrogen in the air is found by subtracting the sum of the volumes of the other components of the air.

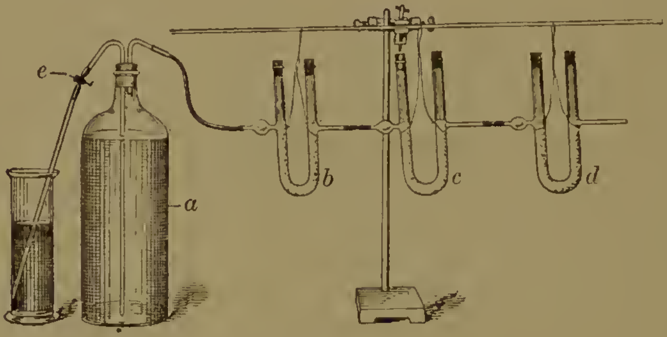

Fig. 34.

When air is thus examined it is found that the quantity of aqueous vapour varies very greatly and irregularly from day to day, and depends on many circumstances, but to a great extent on the *temperature* of the air. Dry air takes up aqueous vapour from water until it becomes *saturated*, and the maximum quantity which may then be present depends on the temperature of the air.*

The percentage of carbon dioxide in the air is not absolutely fixed, but varies so little, if only the air from open country is examined, that the variations are almost within the limits of experimental error. Similarly the percentage of oxygen, although not absolutely constant, varies extremely little in different parts of the world, and so also that of the nitrogen. The composition of dried air from open places is thus practically constant, and is shown in the following table:*

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* One litre of air at 10° saturated with aqueous vapour contains 0·009 g. of water; at 15°, 0·012 g.; and at 20°, 0·017 g. If such saturated air be cooled, a part of the water is deposited in the form of mist, rain, hail, snow, &c., according to circumstances. One cubic mile of air saturated at 35° would deposit about 140,000 tons of water if cooled to 0°.

	By Volume.†	By Weight.†
Oxygen . . .	20·99	23·15 per cent.
Nitrogen . . .	78·03	75·51 "
Carbon dioxide . .	0·03	0·05 "
Other components .	0·95	1·29 "

As fresh air, free from water vapour, is practically constant in composition, so also is the weight of a given volume of such air under fixed conditions; 1 litre of dry air under standard conditions (compare p. 159) weighs 1·293 g., and its density (p. 65) is 14·4.

In studying carbon dioxide and oxygen it was concluded that each of these gases is a definite substance (not a mixture), because different samples of the given gas have constant properties; further, it was concluded that calcium carbonate is a compound because it is constant in *composition.* Now since dry air is practically constant in properties and in composition (the slight observed differences might be due to experimental error), must it be concluded that dry air is a definite compound, formed by the combination of the various gases which can be absorbed from it by the *chemical* methods given above?

In considering this question the first point to bear in mind is, that although samples of air may be taken from widely separated open places on the earth's surface, it is extremely unlikely that such samples would differ in composition even had the air been originally a heterogeneous mixture; it has been circulating during so many thousands or millions of years that it would almost certainly have become homogeneous by this time. In other words, it is only possible to obtain *one* sample of 'fresh' air, and so the fact that this sample is practically constant in properties and composition is of no value as evidence in deciding this question.

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* Owing to the great variation in the percentage of aqueous vapour, analyses showing the composition of air generally give that of *dried* air.

† 'By volume' means that 100 volumes of air contain *volumes* of the various gases in the proportions given. 'By weight' means that 100 g. of air contain the given percentage *weights* of the various gases.

Now it has already been shown that when two substances are merely mixed together, it is sometimes possible to separate them by certain physical processes; such a process may be employed to separate the two gases oxygen and nitrogen, which are the principal components of the atmosphere.

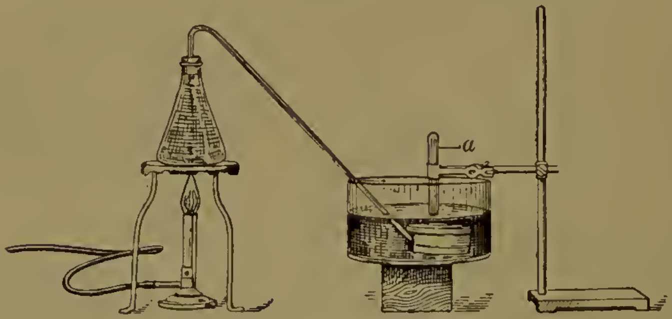

Fig. 35.

When air, freed from carbon dioxide, is shaken with cold water for some time the water dissolves, and finally becomes saturated with, the atmospheric gases; if now a flask (fig. 35) is completely filled with this *solution*, and the bent delivery-tube, which dips under a test-tube (*a*) is also filled with it, then on heating the solution *bubbles* appear long before it begins to boil, and the dissolved gases are expelled because the *solubility* of a gas (p. 66) diminishes as the temperature rises.* The dissolved 'air' may thus be collected. If now a stick of phosphorus is introduced and left in this 'air,' about 35 per cent. by volume is absorbed by the phosphorus, and there remains about 65 per cent. of gas which extinguishes a lighted taper. The mixture of gases expelled from the water contains a much larger proportion of oxygen than does the air, because the solubility of oxygen (p. 85) is greater than that (2·33 at 0°, 1·65 at 15°) of nitrogen.

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* The water from which the gases have thus been expelled has a 'flat,' insipid taste.

The two principal components of the air may thus be separated to some extent by taking advantage of a difference in their solubility (fractional solution), just as two solid components of a mixture may sometimes be separated by fractional crystallisation (p. 32).

This fact shows that the oxygen and nitrogen are probably mixed and not combined together;* further experiments confirm this conclusion.

One of the most obvious characteristics of chemical change is the complete disappearance of all the specific properties of the substances which take part in the change and the appearance of a set of totally new properties in the products. When, for example, oxygen combines with a solid element, such as copper or phosphorus, the properties of the product have not the slightest resemblance to those of its constituents; and it is shown later that this is equally true when oxygen combines with a gaseous element.

Now if a cylinder divided into five equal volumes is filled with and inverted over water, oxygen prepared by any of the usual methods can be bubbled up into the cylinder until one-fifth of the water is displaced. The mouth of a jar containing the gas (nitrogen) which remains after iron has rusted in the air may then be brought under the cylinder, and the rest (four-fifths) of the water displaced by this gas. No sign of change is observed. The cylinder now contains something which is very much the same as ordinary 'air;' something in which a candle burns just as it does in air; something which has physical and chemical properties such as would be expected of such a *mixture* of the two gases, and which would not be appreciably altered if a little more of either gas were added to it.

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* There is an alternative conclusion if the results of this experiment only are considered, namely, that the gases are really combined, but that the compound which they form is decomposed by water. This alternative is conclusively disproved by other evidence.

For reasons such as the above, and for many others of more importance which are given later (pp. 168 and 270), it is concluded that the oxygen and the nitrogen of the atmosphere are not combined, but are merely *mixed* together.

In addition to the gases already mentioned, the atmosphere contains minute quantities of other components, such as sulphur dioxide (p. 229), hydrogen chloride (p. 142), and hydrogen sulphide (p. 216), which are produced in fires, manufactories, and so on; also traces of ammonia (p. 260) or ammonium nitrate, and possibly ozone and hydrogen peroxide.

Mineral dust and living particles (pollen, spores, germs, bacteria) are also present in the air, and many of the last-named play an important part, beneficent or baneful, in the world's economy.

Several other matters in connection with the atmosphere are dealt with later (pp. 138, 139).

CHAPTER XIII.

Hydrogen and Water.

When sulphuric acid (p. 39), diluted with water, is poured on to some iron filings contained in a test-tube a vigorous effervescence is observed owing to the escape of an invisible gas, and if a lighted taper be applied to the mouth of the tube a 'pop' is heard and the gas takes fire; it is combustible. An invisible combustible gas is also liberated when zinc or magnesium (but not when copper, mercury, or silver) is treated with *dilute* sulphuric acid; further, such a gas is also liberated when iron, zinc, or magnesium is treated with hydrochloric acid (p. 39).

Observations of this nature were made by Cavendish about 1766, and he named the gas 'inflammable air.'

In order to study this gas, one of the given metals, generally granulated zinc,* is placed in an apparatus similar to that used in preparing carbon dioxide (fig. 19); the acid is poured down the funnel (*a*)* and the gas is *collected over water*. The first cylinder of gas is not used, as it also contains air and the mixture is explosive.

The gas is colourless, and, when prepared from good samples of metal and of acid, it has no smell. Impure materials give a gas which has a disagreeable odour caused by small quantities of other gases (impurities).† The gas does not seem to dissolve in water, but careful experiments show that its *solubility* (p. 66) is 2·14 at 0°, 1·87 at 15°.

The gas burns when a lighted taper is put to it; it is inflammable and combustible, but the flame is almost invisible in daylight, and practically *non-luminous*. A lighted taper pushed right into the gas is immediately extinguished.‡

When a jar of the gas is left open for, say, thirty seconds and then tested with a lighted taper, it is found that the gas has escaped; but when a jar of the gas is held mouth downwards for an equal length of time and then tested, the presence of the gas is shown. The gas therefore is lighter than air, into which it rises as a cork rises in water.

In doing these experiments a mild or vigorous explosion is almost certain to occur when the lighted taper is placed to the gas, and it is noticed that this explosion is more vigorous when the gas has had an opportunity of mixing with the air. When a sound soda-water bottle about one-quarter filled with water and three-quarters with air is inverted in a trough and the water is displaced by the gas, there results a mixture of air and gas which explodes violently when ignited.

That the inflammable gas is lighter than air can be shown in many other ways; for example, the gas may be *poured* upwards. A small jar (*a*) containing air is held upside-down just above the table, and a larger jar (*b*) of the gas is brought close to it as shown (fig. 36); the closed end of (*b*) is then slowly brought downwards, as indicated by the arrow, to the position (*c*), and (*a*) is closed with a glass plate. On testing (*a*) with a lighted taper it is found to contain some of the gas, whereas the contents of (*b*) do not ignite.

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* Compare footnote on quantities († p. 62).

† Ordinary commercial metals, acids, and other substances are seldom pure (p. 33).

‡ The jar of gas is held *upside-down* in showing that the gas extinguishes a lighted taper.

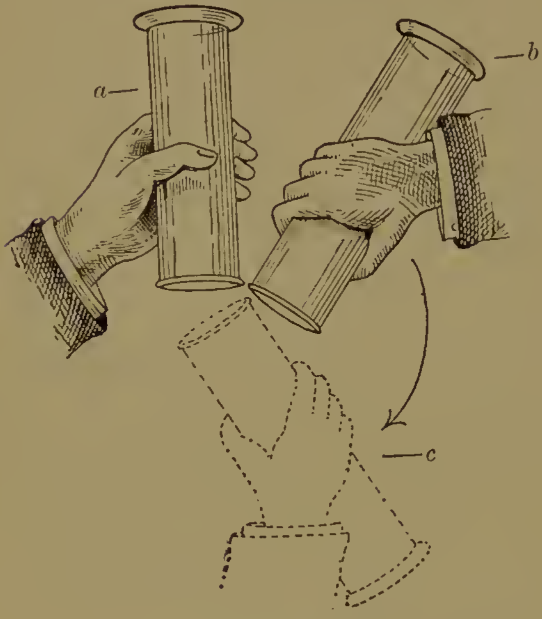

Fig. 36.

A large beaker may also be suspended upside-down from one arm of a balance and counterpoised; some of the gas may then be poured upwards into the beaker, which rises as the air is displaced by the lighter gas.

Balloons of very thin india-rubber, or of collodion, filled with the gas, rise in the air; so do soap-bubbles blown with the gas. The gas in the bubbles may be ignited as the bubbles ascend.

Different samples of the gas obtained by using any of the metals already mentioned, and either of the acids, show the qualitative properties described above. When such samples are carefully washed (p. 67), further purified if necessary, and dried (p. 67) they are found to be identical in every respect; they have all exactly the same solubility in water: a litre of every sample measured under standard conditions weighs exactly 0·0899 gram. These facts, and many others given later, show that the gas is fixed and constant in properties; it is a definite substance and not a mixture. It has never yet been decomposed; it is an element, and is called **hydrogen** (p. 105). Hydrogen is the lightest substance known, and its *density* is taken as unity, that of all other gases being expressed in terms of this standard; it is 240,000 times lighter than an equal volume of platinum. It is known to exist in the sun's atmosphere.

The fact that all the three metals named above (and others as well) give rise to hydrogen when they are treated with dilute sulphuric or hydrochloric acid might be accounted for by assuming (1) that hydrogen is contained in all the metals, and that the acid sets it free or liberates it, just as acid liberates carbon dioxide from calcium carbonate; (2) that the hydrogen is contained in both the acids named, and that the metals set it free; (3) that the hydrogen is set free from the water in which the acids are dissolved.

As it has already been stated that the metals are elements, it is obvious that the first of these assumptions can be shown to be untrue. How this might be done may be indicated.

In the preparation of hydrogen by any of the above methods the metal disappears entirely if sufficient acid is used,* and on evaporating the solution a substance totally different from the metal is obtained in crystals; thus the solution obtained from iron and sulphuric acid gives crystals of *green vitriol* (p. 226); that from zinc and sulphuric acid, *white vitriol.* The metal, therefore, has been changed, and has dissolved chemically in the acid. Now the weight of the substance formed is far greater than that of the metal used; some matter has combined with the metal. This does not prove that the hydrogen cannot have come from the metal, because the metal might have gained more matter by combination than it lost by the liberation of the hydrogen; but it can be proved that the product, green vitriol, for example, contains (in a combined form) the *whole* of the metal which was used, since the *whole* of that metal may be obtained again from the green vitriol by certain processes in which no hydrogen or compound of hydrogen is employed.

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* When impure metals are used relatively very small quantities of *insoluble* black particles often remain. These cannot be the metal; they are separated by filtration.

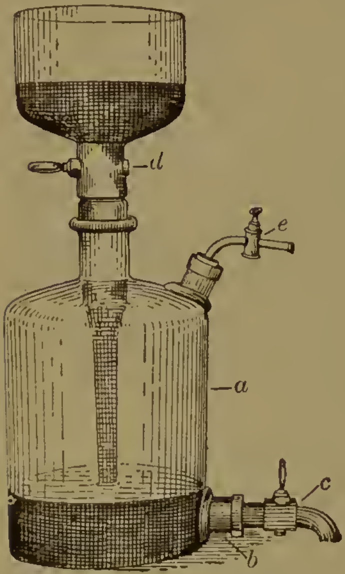

Fig. 37.

As to the second and third assumptions regarding the origin of the hydrogen, the fact that water and metal do not give hydrogen until the 'acid' is added *seems* to indicate that the gas comes from the latter; this inference is shown to be correct by experiments to be described later (footnote *, p. 146).

WATER.

When hydrogen, prepared by any method and conveniently contained in a *gas-holder* * (fig. 37), is passed successively through, say, three tubes (*a*, *b*, *c*, fig. 38) containing anhydrous calcium chloride, all water vapour is absorbed, probably by (*a*) alone.† When it is thought that the air has been displaced from the apparatus a test-tube is inverted over the outlet (*d*) for a minute, and the gas is tested by taking the tube (closed by the thumb in transit) to a Bunsen-flame. If and when the gas takes fire quietly, the hydrogen escaping from (*d*) may be lighted, and a clean, dry gas-jar held over the flame; it is then noticed that the glass jar becomes covered on the inside with a *dew*, which looks like condensed steam. If kept over the flame for some time the jar gets hot, and the dew is then no longer deposited; but if the flame is allowed to play on to a dry retort (*a*, fig. 39), kept cool by a stream of cold water inside, the dew is deposited on the retort and drops of liquid fall into the basin below.* This liquid is tasteless and odourless; it freezes at 0° and boils

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* The chamber (*a*) is filled with water, and the gas is introduced through the tubulure (*b*), the displaced water running out; this tubulure is then stoppered with the tap (*c*). When a stream of the gas is required the tap (*d*) is opened; the pressure of the water drives the gas through the outlet tube on opening the tap (*e*).

† If (*c*) is weighed before and after the experiment it should show no increase in weight, proving that only dry gas has passed through it.

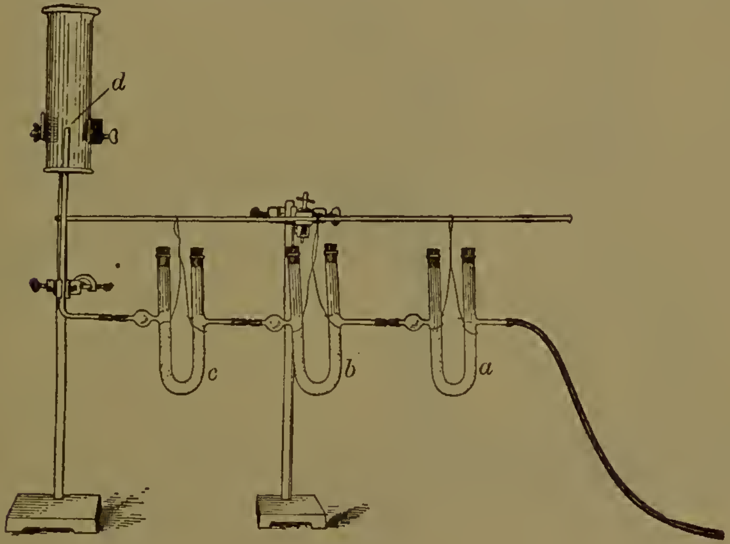

Fig. 38.

at 100°; 1 c.c. of it at 4° weighs 1 gram; when added to anhydrous copper sulphate (p. 36) the latter turns blue; when poured over quicklime slaking occurs. The liquid, therefore, is *water*. Water is obtained when *dry* hydrogen burns in the air.

It seems hardly possible that this water can have been obtained by the condensation of the water vapour in the air, because the air is *heated* by the flame of the burning gas; nevertheless, the experiment may be repeated, using *dried* air as well as dried hydrogen.

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* The end of the tube at which the gas is burnt is made of platinum, as glass melts after some time in the hot flame.

For this purpose a stream of air dried with the calcium chloride tube (*a*, fig. 40) is passed through the chamber for some time, (*b*) and (*c*) being closed with corks, and then a burning jet of *dry* hydrogen is inserted at (*b*) as shown; water is obtained as before, and collects in the calcium chloride tube (*d*), which may be weighed before and after the experiment. Sulphuric acid is used to dry the gas (p. 67).

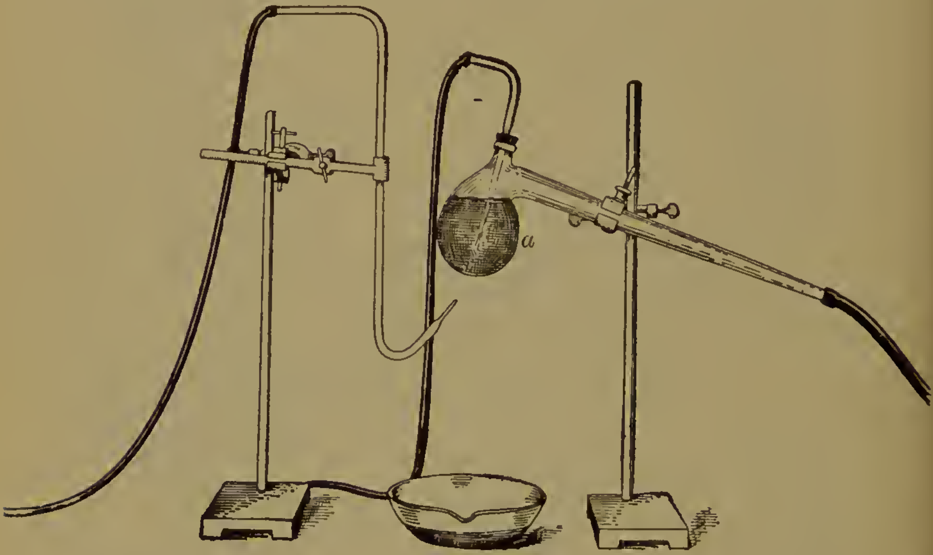

Fig. 39.

It is thus proved that water is *formed* or *produced* when *dry* hydrogen is burnt in *dry* air.

Now it has been shown that in certain other processes of 'burning' the burning substance combines with the oxygen of the air. Is this so in the case of hydrogen, and is the product, water, a compound of hydrogen and oxygen? If so, dry hydrogen should burn in dry oxygen, forming water, and both the elements, as gases, should disappear.

This conclusion may be tested in the following manner.

Firstly, dried hydrogen is burnt in dried oxygen in the apparatus already shown (fig. 40); the flame is larger and brighter than when air is used, but otherwise the results are similar: water is formed. A jet of burning hydrogen is now introduced into a narrow bell-jar filled with oxygen (fig. 41), the cork (*a*) fitting tightly; as the hydrogen burns the water rises in the bell-jar, showing that oxygen as well as hydrogen is being used up.

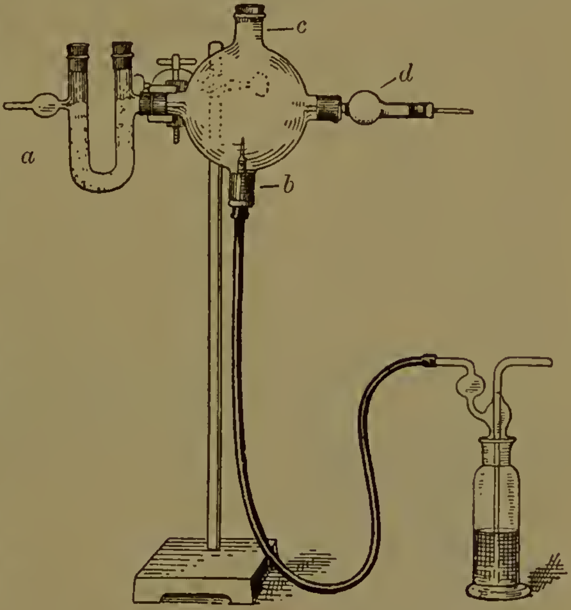

Fig. 40.

It is thus proved that water is a *compound* of hydrogen and oxygen; its *synthesis* (p. 73) from these two elements was first accomplished by Cavendish in 1781. The name hydrogen (which signifies water-producer) was given to this gas by Lavoisier.

When *dry* copper oxide is heated in a stream of *dry* hydrogen a liquid is obtained.

The copper oxide is placed in a tube, and hydrogen, carefully dried with calcium chloride, is passed through the tube; after it is proved that the air has been expelled (p. 102) the copper oxide is heated. The black powder changes and copper appears; after some time a liquid is deposited on the colder parts of the tube, and may be collected; it can be proved that this liquid is water. This is another *synthesis* of water.

This experiment also shows clearly that one element may withdraw another from a compound of the latter; copper oxide does *not* change when it is heated alone or in air, but when it is heated with hydrogen, water is formed by the combination of the oxygen and hydrogen. If, instead of copper oxide, some litharge (oxide of lead) or oxide of iron is used a similar result occurs, and the oxide is said to be *reduced* to the metal. Hydrogen, however, does not reduce all oxides under such conditions.

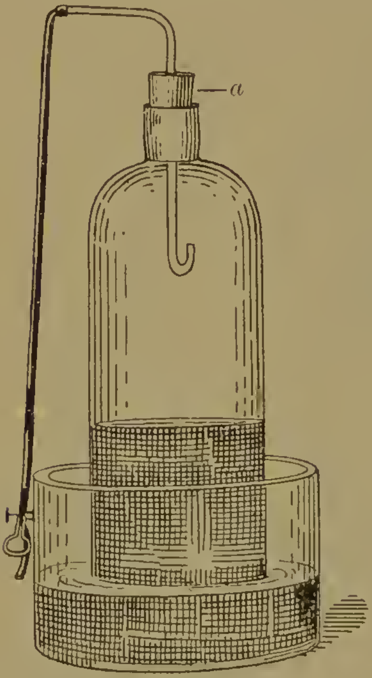

Fig. 41.

There are many other ways in which water may be formed; in fact, this compound is very generally produced when substances containing *combined* oxygen are 'treated' with those containing *combined* hydrogen under suitable conditions (pp. 147, 224).

The *decomposition* of water was first accomplished by Lavoisier (1783), who found that hydrogen is liberated when water vapour (steam) is passed over red-hot iron. Apparatus suitable for this experiment is shown in fig. 42. Steam, generated in (*a*), passes through the iron tube (*b*), which contains iron nails heated to redness; when a gas-jar filled with water is inverted over the delivery-tube (*c*) it is rapidly filled with a gas, which can be proved to be hydrogen. On examining the nails after the experiment they are found to be coated with a black substance, and if they are carefully dried and then heated in a stream of dry hydrogen water is obtained and iron remains.

It is thus shown that iron decomposes water at a red-heat, hydrogen and oxide of iron being produced; also that hydrogen decomposes oxide of iron at a red-heat, iron and water (oxide of hydrogen) being formed. This is another example of a reversible chemical change (p. 86).

Some other metals decompose water at high temperatures—magnesium, for instance. If a piece of magnesium ribbon, burning in the air, is dipped into a flask from which steam is escaping rapidly, the magnesium continues to burn in the steam; it decomposes the compound water, forming magnesium oxide and hydrogen, and as the hydrogen escapes into the air it also takes fire and combines with atmospheric oxygen, forming water again. Some metals, such as sodium and potassium, decompose water and liberate hydrogen when they are thrown on to cold water;* the metal disappears, and there is formed a solution of caustic soda (p. 78) or caustic potash (p. 79), as the case may be. Copper does *not* decompose steam.†

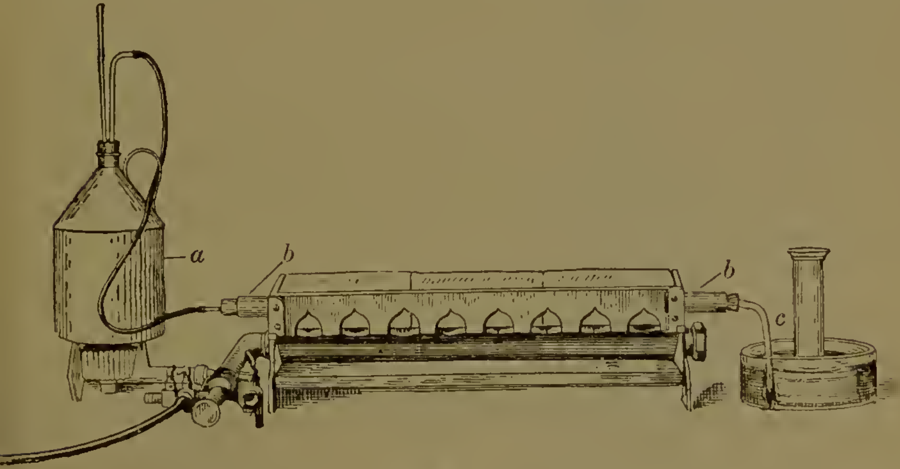

Fig. 42.

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* The student should not try this experiment except under supervision, otherwise dangerous accidents may happen.

† Although metals as a class have certain properties in common, each metal is a distinct element, and as the behaviour of one element cannot, as a rule, be foretold from that of another, it is necessary to be very careful in drawing any conclusions based on analogy—that is to say, on a probable

It is also possible to obtain both hydrogen and oxygen from water in a single experiment by making use of an electric current. The apparatus shown in fig. 43 is called a voltameter. Water, to which a few drops of sulphuric acid have been added, is poured into (*a*), and the taps are opened until the water completely fills the two tubes (*b*, *b*); plates of platinum (*c*, *c*) are fastened to pieces of wire, which pass through the rubber stoppers (*d*, *d*), and are connected with the terminals of a suitable source of electricity (p. 297). When

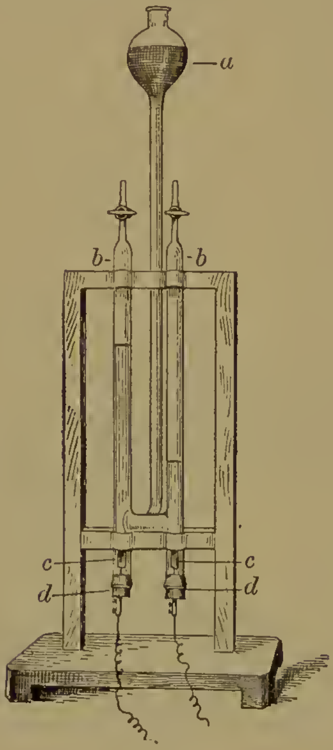

Fig. 43.

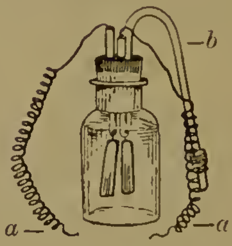

Fig. 44.

resemblance of two elements. Thus, although copper and iron both combine with oxygen to form oxides, and iron decomposes water at high temperatures, copper does not; hydrogen decomposes both these oxides at high temperatures, but does not decompose calcium oxide or magnesium oxide.

the electric current passes bubbles are seen to form on the platinum plates and rise in the tubes; after some time both tubes contain colourless gases, but in one the volume of the gas is just twice that in the other. The gas of which there is the larger volume can be identified as hydrogen, the other as oxygen. The water has been decomposed into its elements; its qualitative *analysis* (p. 73) has been completed.

Instead of collecting the two gases separately, they may be collected together. The wires (*a*, *a*, fig. 44) through which the electric current is conducted pass through glass tubes filled with sealing-wax, and are connected with the platinum plates, which are immersed in the acidified water. The mixture of two volumes of hydrogen and one volume of oxygen, which escapes through the tube (*b*), is called *electrolytic gas*, and is extremely dangerous, since, when it is heated or ignited, the elements combine instantaneously and a very violent explosion results. The explosion is much more violent than in the case of a mixture of hydrogen and air, because there is no nitrogen present to damp or hinder the (chemical) combination.

The explosion of electrolytic gas is most safely shown by letting the gas bubble through some soapy water contained in a very shallow vessel or on the palm of the hand. When some soap-bubbles have thus been formed and the apparatus removed to a safe distance the gas in the bubbles may be ignited with a taper.

Percentage Composition of Water.—The quantitative analysis of water can be made in many ways. The principle of one important method is as follows: A large *weighed* quantity of dry copper oxide is placed in a tube and heated in a stream of dry hydrogen, as described already; some of the copper oxide is reduced (p. 106), and water is formed; the water is collected in weighed tubes containing calcium chloride. After some time the operation is stopped, and the weight of the water which has been produced is ascertained by weighing the calcium chloride tubes; the mixture of copper and copper oxide is weighed, and the weight is subtracted from the original weight of the copper oxide; the difference or *loss* gives the weight of the *oxygen* which has been withdrawn by and combined with the hydrogen. The weight of the combined *hydrogen* in the known weight of water thus formed is obtained by subtracting the weight of the oxygen.

Such a method was first employed in 1820 by Berzelius and Dulong, and the result of one of their experiments was: Weight of water, 9·052 g. Loss of weight of copper oxide, 8·051 g. Therefore, 8·051 g. of oxygen has combined with 9·052 – 8·051 = 1·001 g. of hydrogen; hence the percentage composition of water is, oxygen 88·94, hydrogen 11·06. The average result of several experiments was, oxygen 88·90, hydrogen 11·10; and that of a large number of similar experiments carried out by Dumas in 1843, oxygen 88·86, hydrogen 11·14 per cent. The results of more recent experiments give the values, oxygen = 88·81, hydrogen 11·19 per cent.

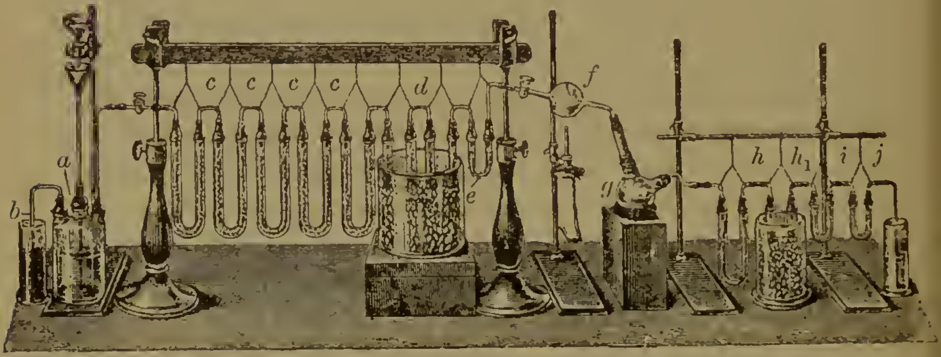

Fig. 45.

In order to obtain accurate results in this, as in other analyses, the greatest care has to be taken. For example, the copper oxide and the hydrogen must be absolutely dry; they must both be pure; every trace of water formed must be collected. For these reasons the apparatus employed by Dumas was rather complicated, as shown in fig. 45 and briefly described below.

Hydrogen is generated in the bottle (*a*), which is provided with a safety-valve (*b*), a tube dipping under mercury. The gas is passed through the tubes (*c*), which contain various substances capable of absorbing known or possible impurities in the gas, and then through the tubes (*d*), which contain phosphorus pentoxide, and are immersed in a freezing mixture to ensure the absorption of every trace of aqueous vapour. The tube (*e*) contains phosphorus pentoxide, and is weighed before and after the experiment; it should *not* show any increase in weight. The bulb (*f*) contains pure dry copper oxide, and is weighed before and after the experiment; the water which is formed is collected in (*g*) and in the two tubes (*h*), (h_1), (the latter being immersed in a freezing mixture,) which are weighed before and after the experiment. The hydrogen in (*f*), (*g*), (*h*), and (h_1) is, of course, displaced by dry air before the second weighing. (*i*) is a weighed tube containing phosphorus pentoxide; if all the water is absorbed in (*g*), (*h*), and (h_1) this tube should not show any gain in weight. (*j*) is filled with phosphorus pentoxide, and serves to prevent atmospheric moisture from entering the apparatus; the outlet-tube dips under mercury.

The close agreement between the results of Berzelius and Dulong, those of Dumas, obtained twenty-three years later, and those of quite recent times, illustrates exceptionally well the law of constant composition or definite proportions (p. 53). The great contrast between the properties of the *compound* water and those of the *mixture* electrolytic gas also affords a good opportunity of noting the great differences which may exist between a compound of two gaseous elements and a mere mixture of the two. Although water vapour or steam resembles electrolytic gas in being 'gaseous,' most of its properties are absolutely different from those of the mixture.

Water in Nature.—The great abundance of water (it covers about three-quarters of the earth's surface), its presence in the atmosphere, in the soil, and in all animal and vegetable organisms, render it one of the most important and best-known compounds. Its physical constants have already been dealt with, and also its action as a solvent (p. 20).

When aqueous vapour, formed by the evaporation of sea- or fresh-water, becomes condensed into rain, the liquid thus formed is probably very nearly pure—it has been distilled (p. 13). But as the rain falls through the atmosphere it dissolves some of the gases, more especially carbon dioxide, oxygen, and nitrogen; solid matter—dust (p. 98)—is also dissolved or brought down mechanically. As soon as the rain reaches the earth it begins to take up other impurities, for although the materials composing rocks and soils (p. 290) are only, as a rule, very sparingly soluble in water, they dissolve, nevertheless, to a slight extent, the physical action of the water being greatly assisted by the previous chemical action of the carbon dioxide which it contains. The water, which then flows into streams or sinks into the earth, perhaps to reappear as well- or spring-water, continues its solvent action, and finally some of it again reaches the sea, and the cycle recommences.

The quantity and the nature of the substances contained in different samples of fresh-water vary very largely, and depend on the nature of the soil or strata over or through which the water has passed. Some of these dissolved substances have a great effect on the behaviour of the water, as explained later (p. 280). Sea-water, although it is continually receiving fresh quantities of dissolved matter, and losing pure water by evaporation, does not seem to alter appreciably in character, and contains about 3·6 g. of dissolved solids in 100 g. of sea-water; its specific gravity is about 1·03 at 0°.

For drinking purposes it is not the dissolved mineral matter contained in ordinary fresh-water which is of so much importance, but the number and the nature of the living organisms or bacteria which may be present; hence the necessity of filtration (p. 22).

CHAPTER XIV.

Carbon.

Charcoal.—When wood has been burning and the fire has died out, there remains a gray powdery material (wood-ashes), and any pieces of wood which have not been thoroughly burnt are blackened or charred where they have been heated; such charred wood, or *charcoal*, has been known from early times, and in countries where wood is plentiful it is prepared by the process known as 'charcoal-burning.' Small logs or billets of wood are built up into heaps and covered with sods or earth, a shaft being left in the middle to serve as a chimney, and small holes at the bottom for the admission of air (fig. 46). The burning is started at the bottom, and the supply of air is then carefully limited, so that the wood only smoulders. After some weeks the fire dies out, and the product is wood-charcoal.

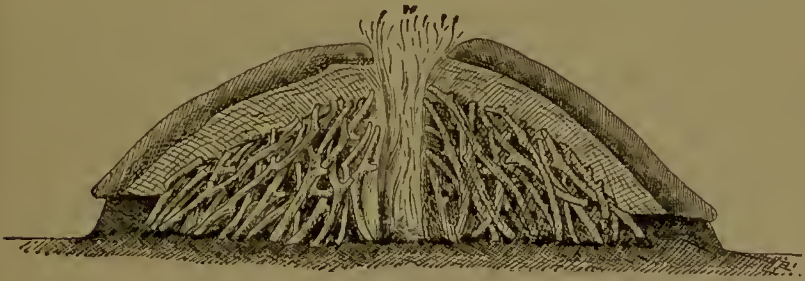

Fig. 46.

Wood-charcoal may be quickly made on a small scale by heating some *dry* chips in an angle-tube (fig. 14, p. 36). At first aqueous vapour escapes, but soon the wood begins to 'char,' and inflammable gases are given off, together with watery and tarry liquids which condense in the receiver (*b*); finally all signs of change cease, and wood-charcoal remains. It is clear that chemical changes have occurred; the materials of which wood consists do not melt or boil, but *decompose.*

Charcoal is sometimes prepared by heating wood in iron retorts in order to utilise the valuable gaseous and liquid products (p. 277).

The term *destructive distillation* is applied to a process such as this in which a compound or a mixture of compounds decomposes, forming a (liquid) *distillate* totally different from the original compound or mixture.

A piece of wood-charcoal has the fortuitous shape of the wood from which it has been prepared, and is *amorphous* (p. 31); it is black, very brittle, very porous, and insoluble in water. When placed in water it floats, because it is buoyed up by the air in its pores; but when the water on which the charcoal is floating is boiled, this air is slowly expelled, and ultimately the charcoal sinks. Its specific gravity is about 1·5.

When a piece of freshly heated wood-charcoal is passed up into a tube containing a dry gas confined over mercury, the volume of the gas diminishes; the gas is absorbed by and 'condensed' in the pores of the charcoal. When the charcoal containing it is heated in a vacuum the absorbed gas is given up again, and as both the charcoal and the gas are thus recovered unchanged, and as the volume of the gas absorbed is *indefinite*, and depends on the physical state of the charcoal, it is supposed that chemical union does not occur; the gas is said to be occluded.* On account of this property, charcoal is used in hospitals and elsewhere for absorbing noxious gases.

It is well known that charcoal burns in the air without smoke, leaving a gray, incombustible powder known as *ash.* The quantity of this ash is easily estimated by heating a weighed quantity of the sample, and weighing the residue until constant. The percentage *varies* from 0·5–4·0 with different samples of charcoal. Now when charcoal is heated, even very strongly, out of contact with the air, it does not burn or change in any way. The filaments which are made white-hot in the ordinary electric lamps are charcoal, but they do not burn because all the air has been pumped out of the bulb. It may be inferred, therefore, that the burning of charcoal is caused by its combination with some gas—probably the oxygen—of the air, and also, since part of it (the ash) does not burn, that charcoal is not homogeneous.

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* 1 volume of charcoal may absorb (occlude) as much as 9 volumes of oxygen, 85 volumes of hydrogen chloride (p. 142), or 90 volumes of ammonia (p. 260) at ordinary temperatures and pressures; at very low temperature absorption is so complete that almost perfect vacua may be obtained.

When a piece of dry charcoal is kindled and plunged into a jar of dry oxygen, it burns much more vigorously than in the air; as a rule the sides of the jar become temporarily covered with a film of moisture, a fact which shows that charcoal contains (combined) hydrogen (p. 103). When the gas remaining in the jar is shaken with lime-water the solution becomes milky, and it can be proved that this is due to the precipitation of calcium carbonate; the jar, therefore, contained *carbon dioxide*. Now it is possible, by the method described later, to collect and weigh the carbon dioxide which is formed when a known weight of charcoal is burned in oxygen; it is thus proved that 1 g. of charcoal gives *about* 3 to 3·5 g. of carbon dioxide. This fact shows that carbon dioxide is a *compound*, because it is produced by the combination of some of the charcoal matter with oxygen; moreover, since the weight of this compound and the weight of the ash obtained from a given weight of charcoal vary with different samples, it is also proved that charcoal is not a pure substance.

This discovery that charcoal is not a definite substance is not surprising. Growing plants require mineral food, which is dissolved by water and absorbed by their roots. The wood from which charcoal is made is not a definite substance, and consequently does not give a pure product, even when it is heated until constant out of contact with the air. As charcoal is insoluble, not only in water but also in all other ordinary liquids, it cannot be purified by crystallisation; nor can it be distilled, as it does not even melt when made white-hot. In fact, it cannot be purified by any of the ordinary methods (p. 33), and the only way in which it can be easily changed in the laboratory is by burning it.

Carbon.—Most vegetable substances leave some ash when they are burnt; but a few, which have undergone purification, as, for example, ordinary sugar, leave none. When sugar is heated in an angle-tube (fig. 14, p. 36) out of contact with the air, it gives gases and liquids, and finally there remains a black, brittle substance, rather like wood-charcoal in appearance, which burns in oxygen, forming carbon dioxide. This substance is called *sugar-charcoal.*

Now, as sugar is known to be a pure compound, the sugar-charcoal prepared from it by heating until constant (in absence of air) might also be expected to be a pure substance (p. 69). This is the case. When different samples, prepared with great care at the highest possible temperature, are completely burnt in oxygen in the manner described later (p. 123), and the carbon dioxide is collected and weighed, 1 g. of the charcoal always gives $3{\cdot}\dot{6}$ g. of carbon dioxide. Sugar-charcoal, therefore, is a *pure* substance, because it combines with a fixed proportion of oxygen, forming the compound carbon dioxide. Sugar-charcoal has never been decomposed; it is an element, and is called **carbon.**

Carbon dioxide, one of the most important carbon compounds, is composed of 1 g. of carbon united with $2{\cdot}\dot{6}$ g. of oxygen; its percentage composition, therefore, is carbon 27·27, oxygen 72·73 (p. 125).

Most crude animal and vegetable materials behave like wood when they are heated out of contact with the air, and give residues which consist partly of carbon, partly of mineral matter. Such residues burn, giving carbon dioxide, when they are heated in the air, and leave an incombustible ash. Animal and vegetable matter, therefore, consists of, or contains, *carbon compounds.*

Dried blood heated out of contact with the air gives a residue known as *animal* or *blood charcoal,* while bones yield *bone-black*, a mixture which contains a very large proportion of mineral matter and less than 10 per cent. of carbon. Lamp-black or soot (p. 134) consists almost entirely of carbon.

When a solution of litmus is passed through an ordinary filter-paper, the filtrate is just as highly coloured as the original liquid, because the litmus is in solution and not in suspension (p. 22); when, however, a litmus solution is passed through a charcoal filter, some or all of the colouring matter is retained by the charcoal, which has the remarkable property of absorbing many substances from their *solutions*. This is best shown by adding some animal charcoal to a warm litmus solution, shaking for a few minutes, and then filtering; the filtrate is colourless. This property of charcoal is applied commercially. Coloured impure solutions of brown sugar, for example, are boiled with animal charcoal, whereby the colouring matter is removed. On evaporating the filtered syrup, white sugar is obtained.

Wood-charcoal is used in making gunpowder (footnote †, p. 241), but its principal use is as a fuel.

Coal.—The 'decay' of vegetable matter covered with earth or water—that is to say, out of contact with the air—is in some respects a process similar to charcoal-burning. The compounds of carbon decompose, gases are given off (marsh-gas), the materials darken, and the percentage of carbon in the residue gradually increases. It is in this way that the different varieties of *coal* have been formed from vast deposits of vegetable matter in the course of thousands of years.

Ordinary coal contains from 70 to 90 per cent. of carbon, according to its age; also hydrogen (5–7·5 per cent.), oxygen, sulphur (p. 211), and nitrogen. These four elements are *combined* together, and form, no doubt, a great many different solid compounds. Coal also contains many other compounds, which remain in a more or less changed condition as ash when coal is burnt. This ash, or 'mineral' matter, varies from 1 to 20 per cent. There are many different kinds of coal. *Anthracite* is a 'smokeless' coal which contains 94–98 per cent. of carbon.

When coal is strongly heated out of contact with air, it undergoes destructive distillation (p. 114), its components are decomposed, and the elements contained in these compounds form a great number of new substances. Ordinary coal-gas, a mixture of many gases, is thus produced; also gas-liquor (p. 267) and coal- or gas-tar. The residue, coke, consists largely of carbon, but contains all the ash of the coal.

Graphite.—Several black materials besides coal are found in the earth in relatively small quantities; among others, that known as *graphite.*

Graphite occurs in beds or in separate lumps; it is rather steel-gray than black, often shows a bright lustre, and is sometimes found in large, distinct crystals. It is easily powdered, giving small scales which have a slippery or greasy feel, as they slide over one another freely. For this reason graphite is used as a machinery lubricant in places too hot for oil. It leaves a black streak when drawn across paper, &c. (*grapho*, 'I write'), as its scales easily rub off, and when mixed with fine clay it is used for making so-called 'lead' pencils;* it is also used (under the name of black-lead) for coating iron, as a conductor of electricity, and for making plumbago crucibles. The specific gravity of graphite varies from 2·0 to 2·6, and its crystals are said to be hexagonal.

When finely powdered graphite is strongly heated in an open crucible it does not seem to 'burn,' but on long-continued heating most of it disappears, and a gray or reddish-brown incombustible ash remains, amounting perhaps to about 5 per cent. of the graphite taken. If heated in a glass tube in a stream of oxygen, graphite burns brightly; on passing the escaping gas through lime-water, calcium carbonate is precipitated; hence graphite contains carbon. Quantitative experiments carried out as described later (p. 123) prove that after *allowing for* the 5 per cent. or so of ash or mineral matter, 1 gram of graphite gives about 3·63 grams of carbon dioxide, which corresponds with about $\frac{3{\cdot}63 \times 27{\cdot}27}{100} = 0{\cdot}99$ g. of carbon; graphite, therefore, is impure carbon mixed with some mineral matter.

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* Graphite was once thought to be lead, or to contain lead, as indicated by the name 'black-lead.'

Diamond.—A transparent, sparkling *diamond*, showing a beautiful play of colours, has apparently little in common with graphite or charcoal, and yet a diamond consists of nothing but the element *carbon*, neglecting a minute quantity (less than 0·2 per cent.) of impurity. This is proved as follows: When a diamond is strongly heated in oxygen it burns, forming carbon dioxide; by burning a known weight in a stream of pure oxygen and collecting and weighing the carbon dioxide which is thus formed, it is found that a unit weight of diamond gives $3{\cdot}\dot{6}$ units of carbon dioxide, just as does pure (sugar) carbon, the minute quantity of negligible impurity remaining as 'ash.'

Diamonds are found in South Africa, India, Brazil, and other places, and the natural 'stones' are dull but crystalline (the crystals being generally octahedral). For use as gems they are cut and polished, but as the diamond is the hardest known substance, it has to be polished with diamond dust; its specific gravity is 3·5 to 3·6, and it is the densest known form of carbon.

The three varieties of the element carbon, namely, charcoal, graphite, and diamond, differ from one another in many physical properties, but they are all infusible even at a white-heat, and insoluble in water and acids. Molten iron, however, dissolves carbon, and when iron ores are heated with coke or coal in order to obtain the metal, the latter dissolves amorphous carbon. On cooling, some of this dissolved carbon separates out in opaque lustrous crystals of graphite; under certain conditions, however, a few microscopic transparent crystals of diamond are also obtained, as has been shown by Moissan. Further, when amorphous carbon is heated very strongly out of contact with air it is transformed into a substance similar to graphite. Diamond is also changed into graphite under these conditions.

Since, ignoring possible impurities, charcoal, graphite, and diamond all consist of one and the same kind of matter, namely, the element carbon, why have they such very different physical properties? As the impurities, if any, could hardly cause these differences, it may be supposed that the particles of the carbon matter are arranged or disposed differently in the three varieties, the amorphous form having no definite or geometrical structure (compare p. 214).

CHAPTER XV.

Some Compounds of Carbon.

Carbon Monoxide.—The gas carbon dioxide, which is so easily prepared from calcium carbonate (p. 62), and which is formed when any variety of carbon is burned in oxygen or in the air, undergoes a remarkable change when it is heated with charcoal. This can be shown by slowly passing dry carbon dioxide through a long iron (or glass) tube containing coarsely powdered charcoal, and strongly heated in a furnace; the escaping invisible gas is collected over water, and as it is extremely poisonous, and has no smell by which its presence might be recognised, the greatest care must be taken not to let it escape into the room.* After collecting some jars of the gas in the usual manner, it can be shown that it is inflammable and burns with a beautiful blue, almost non-luminous flame; also that it is practically insoluble in water. This gas is called **carbon monoxide.** Obviously the carbon dioxide has changed, and yet it has been heated with carbon only. As carbon dioxide is not changed when it is passed through a hot empty iron tube, it may be inferred that carbon dioxide and carbon combine together, or that some of the oxygen in carbon dioxide is taken away by the red-hot carbon.

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* Many fatal accidents have occurred with this gas, and its preparation should only be undertaken by an experienced person, preferably in a good draught chamber.

The sample of gas obtained in the manner described above will almost certainly precipitate calcium carbonate when it is shaken with lime-water; this might be expected, as it is not improbable that some of the carbon dioxide may have escaped contact with the carbon. In order to remove any unchanged carbon dioxide, the gas may be passed through tubes containing soda-lime attached to the end of the iron tube. When a jar of the gas thus purified is shaken with lime-water a precipitate is *not* formed; but if the gas is now ignited and the contents of the jar again shaken, a precipitate, which can be proved to be calcium carbonate, is obtained. It is thus proved (1) that carbon dioxide is formed when carbon monoxide burns in the air; (2) that carbon monoxide contains carbon; and since the gas is not carbon only, (3) that it also contains oxygen. As it combines with oxygen to form carbon dioxide, it must contain a smaller proportion of oxygen (a larger proportion of carbon) than does carbon dioxide.

Carbon monoxide may be prepared from several carbon compounds (p. 283). The purified gas obtained by different methods is constant in properties; its density, for example, is always 14, and its *solubility* in water 2·4 at 15°; a given weight of the gas always gives a fixed weight of carbon dioxide when it is burned (p. 122); the gas, therefore, is a definite substance.

Carbon monoxide is often formed in an ordinary coal or wood fire (p. 132) and in charcoal stoves and foot-warmers. When the gases from burning charcoal are not led into a chimney, they may cause fatal accidents; coal-gas is so very poisonous because it contains carbon monoxide.

At a moderately high temperature carbon monoxide, like hydrogen, withdraws and combines with the oxygen contained in copper oxide; the metallic oxide is 'reduced' and carbon dioxide is formed by the 'oxidation' of the monoxide. As the percentage composition of carbon dioxide is known, that of carbon monoxide may be determined by a method very similar to that used in the case of water (p. 109). The dry gas is passed over a weighed quantity (excess) of heated copper oxide, and the carbon dioxide is collected in weighed tubes containing soda-lime; the loss in weight of the copper oxide gives the weight of oxygen which has combined with the carbon monoxide.

The following example shows how the composition is calculated from the result: Weight of carbon dioxide collected, 17·606 g. Loss in weight of copper oxide = weight of oxygen, 6·401; therefore the weight of carbon monoxide which has combined with 6·401 g. of oxygen is 17·606 − 6·401 = 11·205 g. Now carbon dioxide contains 27·27 per cent. of carbon and 72·73 per cent. of oxygen (p. 125); therefore 17·606 g. contain $\frac{17{\cdot}606 \times 27{\cdot}27}{100} = 4{\cdot}801$ g. of carbon and $\frac{17{\cdot}606 \times 72{\cdot}73}{100} = 12{\cdot}805$ g. of oxygen. As the whole of the carbon was already present in the carbon monoxide burnt, 11·205 g. of this gas consist of 4·801 g. of carbon and 6·404 g. of oxygen. The percentage composition of carbon monoxide is thus found to be, carbon = 42·85, oxygen = 57·15, a result which has been established by many analyses.

Sugar.—Common sugar, which is obtained from the sugar-beet and from the sugar-cane, is a well-known colourless, crystalline substance, readily soluble in cold water and having a sweet taste. When gently heated it changes its state and melts, but at higher temperatures it decomposes and chars (p. 116). The fact that carbon is obtained when pure dry sugar is heated in absence of air proves that sugar is a compound of carbon; the liquid product, which is also formed in this process, is a mixture, from which by fractional distillation and other methods *water* may be isolated; hence sugar contains the elements hydrogen and oxygen as well as carbon.

Now when sugar is heated in a glass tube through which a stream of oxygen is being passed, the sugar burns brightly and there is no residue of carbon; the escaping gas contains carbon dioxide and water vapour, a fact which shows that the carbon matter and the hydrogen matter in the compound sugar have combined with a fixed proportion of oxygen and formed the compounds carbon dioxide and water. If, therefore, a weighed quantity of sugar were completely burnt and these two products were collected separately and weighed, then, as it is known that carbon dioxide contains 27·27 per cent. (or $\frac{3}{11}$) of carbon, and water 11·19 per cent. (or $\frac{1}{9}$) of hydrogen, it should be possible to calculate the weight of carbon and of hydrogen in the known weight of sugar.

A few attempts to analyse sugar in this way would reveal difficulties; it would be found that some of the sugar was decomposed into *volatile* brown or tarry products which passed into the absorbing tubes. In order to prevent this and to ensure *complete combustion*, the weighed quantity of sugar is heated in a stream of *dry* purified air (free from carbon dioxide) in a glass tube which contains red-hot copper oxide. Just as hydrogen and carbon monoxide abstract oxygen from heated copper oxide and are 'oxidised' to water and carbon dioxide respectively, so also do the gaseous and liquid decomposition products of sugar; the consequence is that under these conditions the *whole* of the carbon and hydrogen in the sugar are finally completely converted into carbon dioxide and water respectively (and nothing else). The water thus formed is collected in a weighed calcium chloride tube, and the *dried* carbon dioxide in weighed caustic soda-bulbs; the increase in weight of these vessels is found by weighing again at the end of the experiment, and the weight of the water and that of the carbon dioxide are thus ascertained.

The apparatus used for such a process is shown and described in fig. 47.

The tube (*a*, *b*) contains a layer of dry copper oxide (*f*, *f*) kept in position by plugs of asbestos (*e*, *e*), and the weighed quantity of sugar is contained in a small porcelain or platinum 'boat' (*d*), behind which a roll of oxidised copper gauze (*c*) is inserted to prevent tarry products from passing backwards into (*j*). The tube (*a*, *b*) is placed in the furnace (*k*), and is connected to the air-purifying apparatus (*g* contains caustic soda, *h* and *j* pumice soaked in sulphuric acid) and to the weighed calcium chloride tube (*l*) and the weighed bulbs (*m*), which contain strong caustic soda and (at *m′*) dry soda-lime. A stream of air is passed slowly through the apparatus, the copper oxide is heated to redness, and the sugar is then slowly heated until it is completely burnt to carbon dioxide and water.

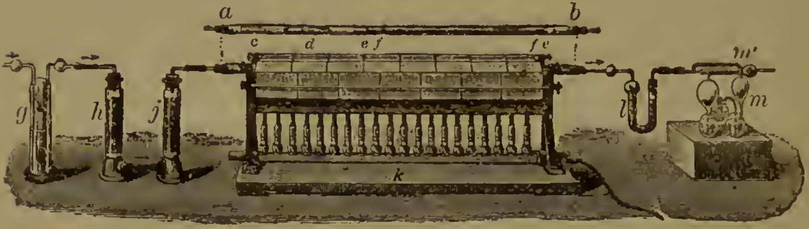


Fig. 47.

From the results of the analysis or *combustion* the percentage composition of sugar may be calculated.

Example.—0·1710 g. of sugar was burnt; weight of water formed 0·0991 g.; weight of carbon dioxide formed 0·2636 g.

Now water contains 11·19 per cent. of hydrogen (p. 110); therefore 0·171 g. of sugar contains $\frac{0{\cdot}0991 \times 11{\cdot}19}{100}$ g. of hydrogen, or $\frac{0{\cdot}0991 \times 11{\cdot}19 \times 100}{100 \times 0{\cdot}171} = 6{\cdot}48$ per cent.

Carbon dioxide contains 27·27 per cent. of carbon (p. 125); therefore 0·171 g. of sugar contains $\frac{0{\cdot}2636 \times 27{\cdot}27}{100}$ g. of carbon, or $\frac{0{\cdot}2636 \times 27{\cdot}27 \times 100}{100 \times 0{\cdot}171} = 42{\cdot}04$ per cent.

It will be seen that the percentage of carbon, *plus* the percentage of hydrogen, is only 48·52; as it is known that sugar also contains the element oxygen (p. 122), and no other element has ever been obtained from it, the *difference*, 100 – 48·52 = 51·48, gives the percentage of oxygen; the composition of sugar, therefore, is, carbon 42·04, hydrogen 6·48, oxygen 51·48 per cent.

The estimation of *one* constituent of a compound in this indirect manner by *difference* is often convenient.

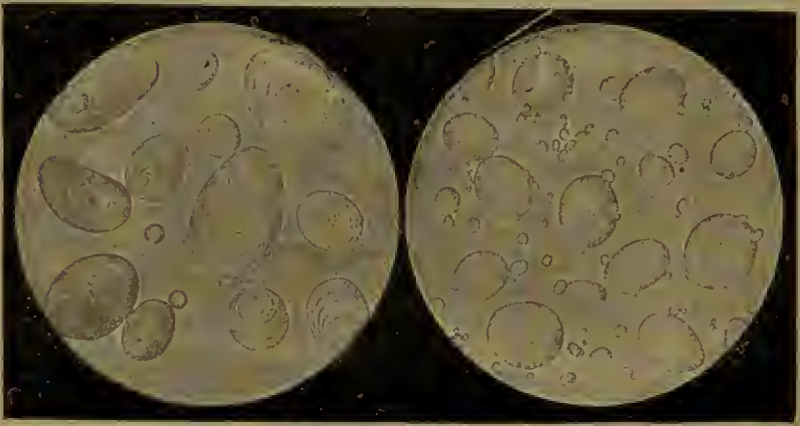
The percentage composition of other (pure) compounds of carbon may be determined by *combustion* in this way.

When oil of turpentine is thus analysed it is found that the percentage of carbon is 88·2, and that of hydrogen 11·8; these values together = 100, and it is thus proved that this oil is a compound of carbon and hydrogen only. Such a compound is called a *hydrocarbon.* Naphthalene and benzene and the gas acetylene are hydrocarbons; petrol and paraffin-wax are *mixtures* of many hydrocarbons; coal-gas, when purified for domestic use, is a mixture of many different hydrocarbons (methane, &c.), hydrogen, carbon monoxide, and other gases.

The weight of carbon dioxide produced from a known weight of sugar-charcoal, wood-charcoal, graphite, &c. is also found by making a combustion in the manner described; it is thus ascertained that 1 g. of *pure* carbon gives $3\cdot\dot{6}$ g. of carbon dioxide, from which result the percentage composition of carbon dioxide is calculated; also that wood-charcoal contains *about* 95 per cent. of carbon and 1 per cent. of hydrogen, as well as *about* 4 per cent. of mineral matter. The percentage of carbon and hydrogen in materials such as wax, tallow, wood, coal, and coke is found in a similar manner.

Starch, like sugar, is a compound of carbon, hydrogen, and oxygen; it occurs in most plants, and is very abundant in cereals (wheat, barley, maize, &c.) and in some tubers (potatoes). It is not crystalline, but occurs in rounded or oval grains, which, under the microscope, have sometimes a very characteristic appearance, so that the starch of one species of plant may often be distinguished from that of another (fig. 48). Starch is insoluble in cold water, and gives a thick paste when it is boiled with water. It burns, and, when pure, leaves no ash.

Alcohol, ethyl alcohol, or spirit of wine has been known (in an impure form) from the earliest times, since it is produced when grapes are crushed and their juice is allowed to stand at ordinary temperatures, the liquid becoming *wine.* The alcohol is formed from sugars which are contained in the grape-juice, these sugars being decomposed into alcohol and carbon dioxide by a plant, *yeast*, which grows on the outside of the grapes; the escape of the carbon dioxide during the decomposition causes a bubbling and frothing, the liquid *ferments*, and the process is called *fermentation.*



Potato Starch. Wheat Starch.

Fig. 48.

Pure alcohol, which can be separated from the water and other substances by fractional distillation (followed by other methods of purification), is a colourless, mobile liquid, miscible with water; it boils at 78°, and dissolves many substances which are insoluble in water (p. 22). It burns in the air with a flame which is only feebly luminous (spirit-lamps), forming water and carbon dioxide; it is composed of carbon

52·2, hydrogen 13·0, and oxygen 34·8 per cent. The intoxicating action of beer, wines, and spirits is due to the alcohol they contain.

Methyl alcohol, or wood-spirit, or wood-naphtha is one of the products of the destructive distillation of wood (p. 277); it boils at 66°, and is very like ordinary alcohol (ethyl alcohol) in its properties; it is composed of carbon 37·5, hydrogen 12·5, and oxygen 50 per cent.

Methylated spirit is a mixture of ethyl alcohol, water, and *crude* wood-spirit.

CHAPTER XVI.

Combustion.

All those materials, such as coal, coke, charcoal, paper, oil, wax, tallow, spirit (alcohol), petroleum,* coal-gas, &c., which are used in daily life for generating heat (fuels) or light (illuminants) by their combustion, are of vegetable or animal origin; as has been already stated, most of them give a residue containing carbon when they are strongly heated out of contact with the air, and when heated in the air they 'burn away,' some of them leaving an incombustible residue or ash (mineral matter). That they all contain carbon is easily proved by burning them separately in gas-jars containing air or oxygen, and then testing the contents of the jar with lime-water;† in every case a precipitate of calcium carbonate is formed. That they all contain hydrogen is also proved in a simple manner; on burning a tallow or wax candle, an oil, spirit, or petroleum lamp, or a piece of dried paper in a dry gas-jar, a dew or film of water is deposited.

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* Petroleum, like coal, is obtained out of the earth, and is often called mineral oil, but it may be of vegetable or animal origin nevertheless.

† Although the air contains carbon dioxide, the quantity of this gas is so small that lime-water, shaken in a gas-jar containing a small volume of air, is hardly changed; it is only when lime-water is left freely exposed to the air that it slowly gives a perceptible precipitate.

Such ordinary combustible materials may also be analysed quantitatively as already described (p. 123), and thus proved to contain carbon and hydrogen, generally also oxygen (by difference), and ash.

Since burning or combustion proceeds in oxygen, and more rapidly than in air, and immediately ceases if the burning material is plunged into nitrogen, it must be concluded that ordinary 'burning' is a process in which compounds of carbon and hydrogen, or of carbon, hydrogen, and oxygen, decompose and combine with atmospheric oxygen, forming carbon dioxide and water.

This conclusion may be confirmed in many ways.

A burning candle placed under a dry bell-jar resting on a glass plate soon 'goes out,' because the jar contains a limited quantity of oxygen; carbon dioxide is formed, as may be easily proved, and dew is seen on the inner surface of the bell-jar.

When a burning candle is placed in a basin floating on water and covered with a bell-jar, the flame soon goes out, because the candle cannot burn when the proportion of oxygen falls to about 16 per cent.; the diminution in volume of the enclosed air, therefore, is not nearly so great as in the case of burning phosphorus (p. 91), and, moreover, carbon dioxide is produced in the place of *some* of the oxygen.

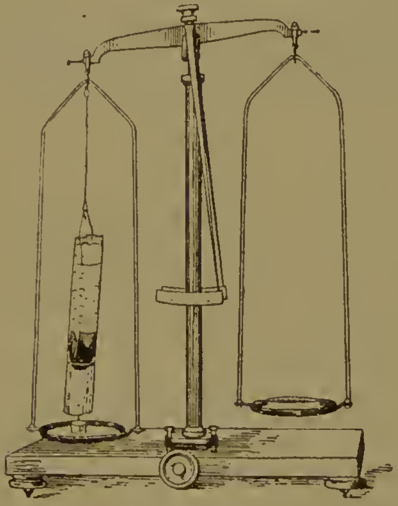

Fig. 49.

If a candle is placed under the glass cylinder (fig. 49), which is loosely filled with soda-lime (p. 79) supported by copper gauze, and, after being counterpoised, the candle is lighted, the pan on which the candle and cylinder are placed soon *descends;* the carbon dioxide and water which have been formed are retained by the soda-lime, and the sum of the weights of these products is greater than the sum of the weights of the materials which have been burnt.

Similar experiments may be performed with other ordinary combustible materials, with similar results.

During many years the phenomena of combustion were summarised and explained on the basis of a hypothesis which, first put forward by Becher (1635–81), was developed by Stahl (1660–1734), and was known as the Phlogistic Theory. It was supposed that all combustible materials contained something which was called phlogiston, and that burning was caused by or resulted in the escape of this phlogiston, the ash, if any, which remained consisting of dephlogisticated (without phlogiston) matter. Materials such as charcoal, which leave very little ash, were thought to be rich in phlogiston, whereas those such as lead and tin, which when heated (in the air) give large residues (or calxes), were thought to contain very little. When a calx such as litharge is heated with charcoal, the metal is obtained; this was explained by assuming that the calx absorbed and fixed phlogiston from the charcoal.

The fact that combustion ceased in a confined volume of air was explained by assuming that the air became saturated with phlogiston and could not take up any more from the combustible material. Hence when oxygen was discovered and it was found that combustion took place in this gas more readily than in air, this was supposed to be due to the absence of phlogiston from the gas, and the gas was called by Priestley 'dephlogisticated air' (p. 82).

The quantitative experiments carried out by Lavoisier, some of which have been referred to (p. 88), and those of other chemists, finally led to the abandonment of the Phlogistic Hypothesis (which had served its purpose) and to the adoption of those views on combustion which are held to the present day.

Although it is thus possible to show and to explain the *results* of the burning or combustion of ordinary materials in a simple manner, the changes which occur are in most cases very complex for two reasons: (1) The materials are often mixtures of many different compounds. (2) These compounds, as a rule, are not directly or immediately converted into carbon dioxide and water, but first undergo various other changes or decompositions, caused by the heat, before they come into contact with the atmospheric oxygen. (Compare the results of *heating* sugar, p. 116, and also the description of a candle-flame, p. 132.)

No further explanation need be given, except in regard to one point which may offer some difficulty. Most ordinary combustible substances, such as sugar, even when carefully dried, give rise to water when they are strongly heated out of contact with the air, and therefore contain combined oxygen, as well as carbon and hydrogen. The three kinds of matter of which these elements consist are combined together in a fixed proportion. On heating the sugar in the air—that is, on burning it—the carbon matter and the hydrogen matter are finally completely separated, and each combines with oxygen matter; *some* of this oxygen matter comes from the substance itself, but this is not enough for the united wants of the carbon and hydrogen, and the rest is obtained from the surrounding air.

Since ordinary burning or combustion is thus a rapid chemical change or series of changes in which a development of heat and light occurs, the term *combustion* may be applied to all other occurrences of a like nature; thus the rapid chemical change which occurs when sulphur, phosphorus, iron, copper, or hydrogen is heated in oxygen is also spoken of as combustion. The term combustion, in fact, is used in a very much wider sense, and is even extended to changes such as those which occur when phosphorus or iron combines slowly with atmospheric oxygen at ordinary temperatures (p. 91) although there may be no emission of light; the reason being that the final results of such changes are essentially the same whether they take place rapidly or slowly.

In connection with such changes one of the materials or substances concerned—coal-gas, for example—is spoken of as *combustible*, and the other, if a gas, as a 'supporter of combustion;' it is clear, however, that as combustion is a change in which *two* materials play an equally important part, there is no reason why they should be thus distinguished, and it is equally true to say that *air* (or oxygen) is combustible and coal-gas a supporter of combustion. This will be obvious from a consideration of the following experiment.

A lamp-glass is fitted up as shown (fig. 50, I.), the top being loosely covered with an asbestos card. A rapid stream of coal-gas is then led into the glass through (*a*), and when the air has been displaced the coal-gas may be ignited at the end of the tube (*b*) as shown; if the asbestos card is then removed air is drawn into the glass by the upward current, and the flame at (*b*) is seen to ascend slowly until it reaches the top of the tube, where it continues to burn as shown in the figure (II.) at (*c*). This flame (*c*) is that of air burning in coal-gas; the air is combustible, the coal-gas a supporter of its combustion. The coal-gas escaping from the top of the

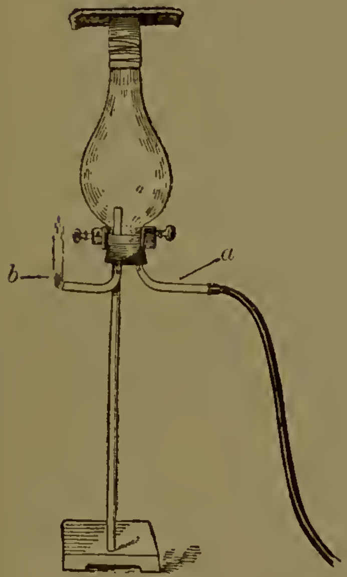

Fig. 50, I.

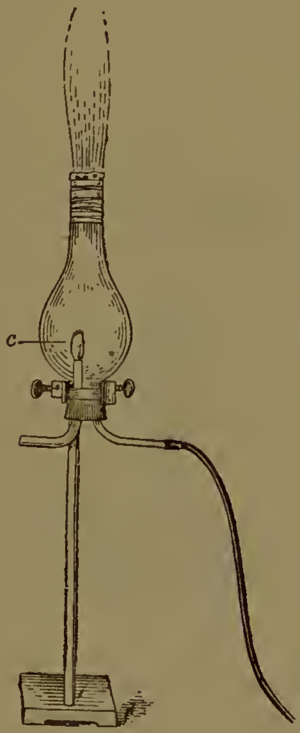

Fig. 50, II.

lamp-glass may be lighted, to show at the same time the flame of coal-gas burning in air.

Flame.—In the burning of copper and of iron no flame is seen; a flame is only formed in the combustion of gases or vapours. In the case of a burning candle, for example, the materials of the wax are first melted and drawn up into the wick, and then decomposed into gases and vapours by the heat of the flame; combustion then takes place all over the surface of this jet of gaseous matter, causing the visible luminous region termed the *flame*. When a small glass tube is fixed in the centre of a candle-flame as shown in fig. 51, some of these gases and vapours pass along the tube and may be ignited at the end (*a*). The cause of flame is also illustrated in an ordinary coal-fire. When the coal is first heated long flames shoot out, because the compounds in the coal are decomposed by heat, giving combustible *gases* and *vapours* (coal-gas); when these compounds have been decomposed the flames die out, because only the solid carbon of the coke or cinders is then burning. After some time, however, if a red-hot, fairly deep layer of cinders has been formed, a beautiful blue flame is seen; this is the flame of carbon monoxide (p. 120). At the bottom of the grate, where the air enters, carbon dioxide is produced; passing up through the red-hot cinders, this gas takes up carbon, forming carbon monoxide, and then when the latter comes into contact with the fresh air flowing over the top of the fire it burns to carbon dioxide. For the same reason a small flame is sometimes seen during the burning of charcoal.

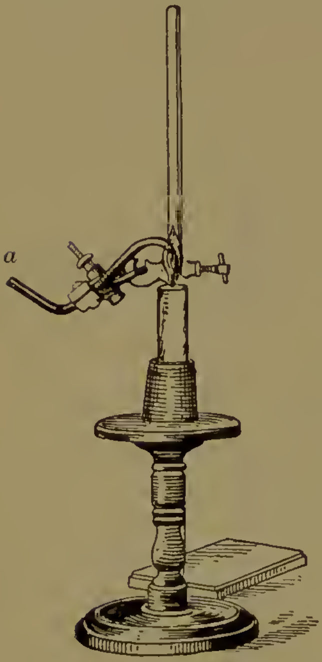

Fig. 51.

Some flames, such as those of burning hydrogen and of burning carbon monoxide, are almost non-luminous,* whereas those of the vapours from wax, oil, and most common combustible materials are yellow or white and luminous, as are also particularly those of burning magnesium and phosphorus. Experiments show that a flame is nearly always non-luminous when it does not contain solid particles, and that the luminosity of a flame may be attributed to the presence of *solid* particles, heated to a high temperature, until they are *incandescent.*

In the flames of burning phosphorus and magnesium (some of the element is converted into vapour) the solid particles of the oxides which are produced are heated to incandescence. In the flames of ordinary materials, such as oil, wax, coal-gas, &c., there are incandescent particles of solid carbon; on passing slowly a clean white plate through such a flame, these particles are cooled, settle on the plate, and blacken it. It can be proved that this deposit of 'soot' consists of (impure) carbon.

The presence of such solid particles in the flames of burning carbon compounds is easily accounted for; most carbon compounds are decomposed when they are heated out of contact with the air, giving various gases and vapours and solid carbon (p. 116). Such decompositions take place within the flame, and as combustion can only go on at the outside, where the jet of gases comes into contact with atmospheric oxygen, the particles of solid carbon inside this jet are merely heated to incandescence until, in their turn, they pass to the outside and undergo combustion.

When the decomposition of the carbon compounds in this way is too rapid, or when the air-supply is limited (which comes to the same thing), some of the carbon particles do not get burnt and are seen escaping from the flame, forming 'smoke.' A little benzene or petroleum burning on an open iron tray gives a very smoky flame, because these substances contain a very large percentage of carbon; by burning tar, turpentine, petroleum, &c. in a limited supply of air and passing the smoke into chambers where it settles, a fine powder (soot) called *lamp-black* is obtained. This consists principally of carbon, and is used in making printer's ink, Indian ink, and black varnishes.

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* The flame of pure hydrogen burning in a *dust-free* atmosphere is invisible, even in the dark.

Simple experiments on flames may be made with a Bunsen-burner (fig. 1, p. 6). When the air-holes at the bottom of the burner are closed the flame is luminous, and deposits soot on any cold object held in it; when the air-holes are opened, the air mixes with the coal-gas escaping from the small aperture (*a*), and by the time the carbon compounds are decomposed in the flame, they are in intimate contact with so much atmospheric oxygen that the carbon is immediately burnt to carbon dioxide or carbon monoxide. If a solid, incombustible substance, such as a piece of platinum wire or a piece of quicklime (wrapped in a loop of platinum wire) is held in a Bunsen-flame, the solid is heated to incandescence and emits light. In the ordinary incandescent gas-light, certain oxides of which the mantle is composed are heated to incandescence in a non-luminous Bunsen-flame. The hotter the flame the greater the incandescence. A platinum wire or a piece of quicklime held in the flame of hydrogen emits more light than in the Bunsen-flame, as the temperature of the former is higher.

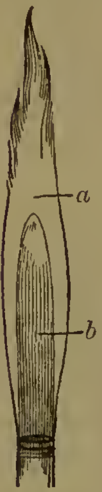

Fig. 52.

When a platinum wire is held across a Bunsen-flame (fig. 52) and moved into different parts, it glows most brightly in the region (*a*) which is the hottest; the inner cone (*b*) of the flame is much colder. The flame of hydrogen or of coal-gas burning in a supply of oxygen is very much hotter than that of the same gas burning in the air, because in the atmosphere there is so much nitrogen, and some of the heat is used up in raising the temperature of this gas; when no nitrogen is present, all the heat developed goes to raise the temperature of the products of combustion. Such a flame, the oxy-hydrogen or oxy-coal-gas flame, may be safely produced with the aid of the blowpipe burner shown in fig. 2 (p. 7); the hydrogen or coal-gas which enters by the tube (*b*) is first lighted, and then the oxygen-supply is connected with the tube (*c*).* The gases do not meet except at the end of the burner (*a*), where they combine without explosion, producing a very high temperature (2000°). Platinum melts in the oxy-hydrogen flame, and a watch-spring held in it burns rapidly, throwing off sparks of melted iron and iron oxide; when the flame is directed on to dry quicklime, the latter glows with an intensely bright light, the Drummond- or lime-light.

Heat of Combustion.—When a fixed weight of a pure substance (element or compound) is completely burnt—that is to say, converted into one or more products of fixed weight—the *quantity of heat* generated in the process is *constant;* thus if 1 g. of pure charcoal is burnt to carbon dioxide the heat developed is 8300 *calories*,† or a quantity which would raise the temperature of 8300 g. of water 1°. Similarly, when 1 g. of pure hydrogen is burnt to water, the heat developed is 34,200 calories. The quantity of heat developed in this way, expressed in calories, is termed the *heat of combustion* of the substance (element or compound).

Now the process known as combustion is merely a very familiar type of chemical change, and it has been found that in *every* chemical change between fixed weights of substances a fixed quantity of heat is developed or absorbed under fixed conditions. As this heat development (or absorption) is generally the result of the union of *two* substances, it cannot be attributed to one of them only; it is a measure of something common to them both, or to the *system*. Hence, instead of saying that the heat of combustion of charcoal is 8300 calories, it is said that the *heat of formation* of a certain fixed weight of carbon dioxide is x calories.*

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* Oxygen and hydrogen, like carbon dioxide, are sold in steel cylinders, into which they are pumped under high pressure.

† A calorie is the quantity of heat required to raise the temperature of 1 g. of water from 4° to 5°.

Now, since heat is a form of energy, and energy, like matter, cannot be created or destroyed, but can only be changed into some other form of energy (heat, light, electrical energy, &c.), the quantity of energy in a given (original) system is different from that contained in the product or products (final system) after a chemical change has occurred under any ordinary conditions; † thus the system [hydrogen 11·2 g. + oxygen 88·8 g.] has far more energy than the product (final system) [water (100 g.)]; the system [carbon 27·3 g. + oxygen 72·7 g.] far more than the system [carbon dioxide (100 g.)]. In order to reproduce the original from the final system in either of these cases, energy (in the form of heat or its equivalent) must be supplied to the final system to an amount equal to that which was dissipated during the chemical change; thus, since the combustion of 11·2 g. of hydrogen gives 34,200 × 11·2 calories, this same quantity of heat or other form of energy is required to obtain 11·2 g. of hydrogen and 88·8 g. of oxygen from water.

Those changes or reactions which give rise to a development of heat are called *exothermic* reactions; if strongly exothermic they generally proceed by themselves when once they have started, as, for example, all ordinary combustions. Changes in which heat is absorbed (that is to say, in which the energy of the final system is greater than that of the original one) are called *endothermic*, and such usually require a continuous supply of heat, without which the change ceases; thus the decomposition of calcium carbonate or of mercuric oxide is an endothermic reaction.

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* The unit of weight adopted in stating the heat of formation of a substance is *not* 1 gram, but 1 gram-molecule (p. 197).

† The law of the conservation of energy, which is based on experimental evidence, may be stated as follows: 'In an isolated, or limited, system, the sum of the various forms of energy remains constant.' Thus if the system hydrogen + oxygen could be so isolated that heat or other form of energy could not escape from or pass into it, then if and when the elements combined the *sum* of the chemical energy and of the heat energy of the final system would be the same as that of the original system.

An *exothermic compound* is one in the formation of which heat is developed, and which therefore requires a supply of energy for its decomposition. An *endothermic compound* requires a supply of energy for its formation, and this energy is given out again in its decomposition.

The development or absorption of heat is not peculiar to chemical change. Physical changes such as the liquefaction or solution of solids, the vaporisation of liquids, &c. are also accompanied by a change in the energy of the system.

Impure substances and mixtures such as coal, wood, coke, &c. have not, of course, a *fixed* heat of combustion; the quantity of heat given out in the burning of unit weight of such materials varies with different samples, and is termed the *calorific value* of the material.

Food—Breathing.—The heat which is generated during the combustion of tallow, oil, sugar, &c. is one of the results of the oxidation of these materials to carbon dioxide and water. These and many other animal and vegetable products, consisting of carbon compounds, which are taken as *food* by animals, undergo similar changes within the body; that is to say, they are finally oxidised by atmospheric oxygen, which is taken into the lungs, and there brought into contact with blood-vessels, through the thin walls of which it passes (diffuses, p. 164), and is then carried by the blood-stream to all parts of the body. The oxidation products, carbon dioxide and water, are returned to the lungs, and pass out of the system at every expiration. Aquatic animals obtain the free oxygen necessary to their life (with the aid of their gills) from the gas which is dissolved in the water. Fish die when placed in cold water from which the dissolved 'air' has been expelled by boiling.

That carbon dioxide is contained in *expired* air in much larger proportion than in the atmosphere is shown with the apparatus (fig. 53). The bottles contain lime-water; applying the mouth to (*a*) and inhaling, air is drawn through the lime-water in (*b*) into the lungs; on exhaling, the expired air bubbles through (*c*), and one deep breath is sufficient to render the lime-water in (*c*) milky, while that in (*b*) shows no perceptible turbidity.

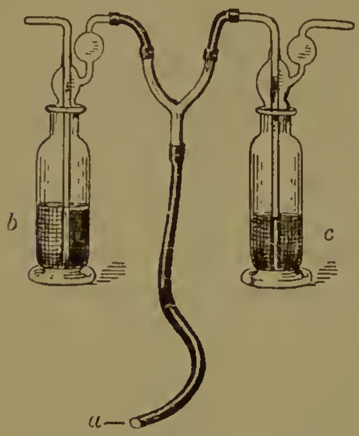

Fig. 53.

The body temperature of living animals is thus kept above that of their surroundings by the combustion or oxidation of compounds of carbon; further, the muscular work which an animal performs is chemical energy, derived from its food, just as the work performed by a steam-engine is derived from its fuel.

Hence the necessity of oxygen to animal life; the nitrogen of the atmosphere passes into and out of the lungs unchanged.

Since expired air contains a much larger proportion of carbon dioxide (namely, 4·4 per cent.) than 'fresh air,' a confined atmosphere in which human beings or animals are living gradually gets changed and becomes 'bad' or 'vitiated,' and the percentage of carbon dioxide in the air of a crowded room may rise to more than ten times that in 'fresh' air. Although carbon dioxide itself is not poisonous except in very large doses, such bad or vitiated air has a very baneful and depressing effect on the human system, probably because it also contains small quantities of disagreeably smelling and poisonous vapours which have been expired; hence the prime importance to health of fresh air and ventilation. The percentage of carbon dioxide in a confined space is also appreciably increased by the combustion of candles, lamps, coal-gas, &c. as illuminants; here again it is probable that small quantities of other products of decomposition are more harmful than the carbon dioxide itself. The products of combustion of an ordinary coal-fire pass up the chimney, and the draught thus caused is an efficient aid to the ventilation of a room.

Living plants, like animals, require a supply of free oxygen, which is absorbed and made use of for the oxidation of carbon compounds. But plants also absorb carbon dioxide from the air during daylight, and within their leaves (which contain a green material called *chlorophyll*) this gas is decomposed into substances containing a smaller percentage of oxygen. These substances, the nature of which is not known with certainty, are retained by the plant as food, and from them the numerous products of vegetable life (starch, sugar, wood, &c.) are produced. The oxygen which is set free in the decomposition of the carbon dioxide passes into the air. This process of *assimilation*, the conversion of carbon dioxide into less highly oxidised materials containing much more chemical energy, is practically the reverse of the changes which occur in the process of ordinary combustion. Energy is stored up in the vegetable products, and its source is the light of the sun ; in the dark this process stops.

As the volume of oxygen given out by plants is greater than that absorbed, it follows that the effect of vegetable life on the composition of the atmosphere is on the whole the reverse of that of animal life. This counterbalancing action, no doubt, plays some part in keeping constant the composition of the atmosphere, but the volume of the latter is so enormous that the effect of either change alone may be regarded as insignificant.

Although animal and vegetable matter is principally composed of compounds of carbon, hydrogen, and oxygen, *nitrogen* is also an important constituent of living matter. The elements sulphur, phosphorus, chlorine, iron, potassium, magnesium, and calcium, in a *combined* form, are also necessary in small quantities to animal and vegetable life.

CHAPTER XVII.

Chlorine and Hydrogen Chloride.

Pyrolusite, a black crystalline material found in the earth, has been known for a long time, and is now called *manganese dioxide.* When this mineral is placed in the flask (fig. 54) and warmed with some hydrochloric acid (compare footnote †, p. 62) a yellowish-green gas is evolved, and the manganese dioxide passes into a soluble substance.* This gas was discovered by Scheele (in 1774), and is named **chlorine** (*chloros*, pale green). It has a very unpleasant and irritating odour, and it is very dangerous to inhale it even when it is largely diluted with air, so that all experiments with chlorine should be carried out in a fume-cupboard. Chlorine is soluble in water (its *solubility* is 237 at 15°), it attacks and combines with mercury, and it is heavier than air; for these reasons it is collected by displacing air upwards, as shown above, and when it is *seen* that the gas-jar is filled, it is covered with a plate smeared with vaseline. Chlorine is non-inflam-

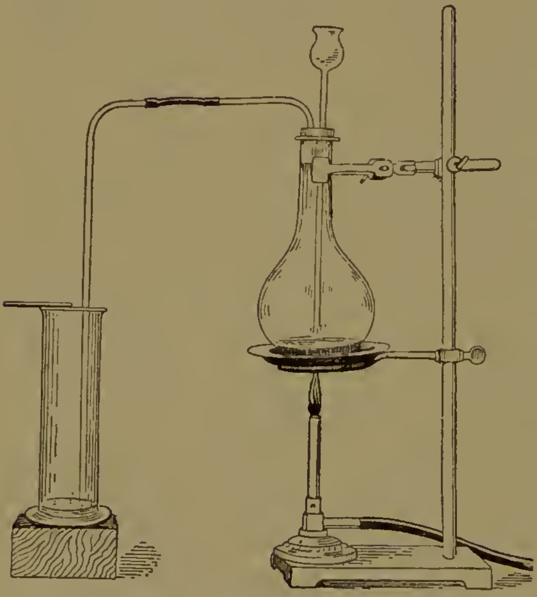

Fig. 54.

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[*] This change is explained later (pp. 209, 286).

mable; a lighted candle plunged into it continues to burn, but with a small, dull-reddish, 'smoky' flame, and the walls of the jar become covered with soot (impure carbon). Many substances take fire spontaneously and 'burn' in chlorine, especially certain metals, when in the form of thin leaf or fine powder; phosphorus plunged into the gas on a deflagrating-spoon (p. 83) takes fire, forming colourless fumes.

When chlorine is prepared in the above manner some 'hydrochloric acid' may be carried over with the gas; for this reason the chlorine may be *washed* with a little water (p. 67), which at first dissolves some of the gas, but soon becomes saturated with it. The hydrochloric acid is present in relatively small quantities, and is so soluble that it continues to dissolve long after the solution is saturated with chlorine. The gas may be dried by bubbling it through sulphuric acid. Chlorine may be prepared in many other ways. The purified gas obtained by different processes is constant in physical and chemical properties, and is an *element;* its density is 35·2.

Chlorine, like oxygen, combines directly with many other elements, and the compounds thus formed are termed *chlorides;* thus *copper chloride* and *phosphorus chloride* are the products when copper and phosphorus respectively 'burn' in chlorine. As already stated, 'burning' in the chemical sense of the word does not imply the presence of oxygen. When litmus solution is shaken with chlorine the colour disappears; and when a piece of calico coloured with any vegetable dye, such as Turkey red, is wrung out in water and then suspended in a jar of chlorine, it is also 'bleached;' when, however, the fabric is well dried and suspended in a jar of dry chlorine, the dye is not attacked. Hence chlorine bleaches, but only when water is present. The reason is given later (p. 285). Many ordinary inks are bleached by moist chlorine, but printer's ink, which consists principally of carbon (p. 134), is not; chlorine does not act on carbon even at high temperatures.

Chlorine is a powerful disinfectant; that is to say, it kills living organisms of all kinds. It is prepared commercially for making 'bleaching powder' (p. 286). The aqueous solution of chlorine has the colour, smell, and bleaching properties of the gas, and is called *chlorine water*.

HYDROGEN CHLORIDE.

It has already been stated that a 'fuming' gas is liberated when sulphuric acid and common salt (sodium chloride) are heated together, and that a solution of this gas in water is called *hydrochloric acid* (p. 39). It is this solution which is used in the preparation of chlorine, and the gas itself may now be studied.

The gas is prepared by gradually adding sulphuric acid to sodium chloride (compare footnote †, p. 62), and suitable apparatus is shown in fig. 54; effervescence sets in immediately, and an invisible gas, which 'fumes' in the air (compare footnote, p. 39), is evolved. As this gas is very soluble in water and rather heavier than air, it is collected by displacing air upwards. When the addition of more sulphuric acid causes no further evolution of gas, the contents of the flask are gently heated; the compound which remains in the flask is referred to later (p. 258).

The gas has no distinct smell, but has a very choking and irritating effect when inhaled; it extinguishes a burning taper (so it is easy to test when a jar is filled) and is non-inflammable.

The solubility of the gas in water is clearly shown by inverting one of the jars of the gas in the pneumatic trough; if the gas is free from air, the water immediately rises and fills the jar.

The gas evolved in presence of sulphuric acid, which is very hygroscopic, is free from aqueous vapour. If prepared from pure materials it is itself pure, and is constant in properties; for example, its density is always 18·1.

It is, therefore, a pure substance, and is called *hydrogen chloride.*

Hydrochloric acid.—When hydrogen chloride is bubbled into water the gas dissolves so rapidly that the bubbles do not reach the surface, and the water becomes warm. If the gas is generated in an apparatus such as that shown in fig. 55, in which the sulphuric acid is dropped on to the salt from a *stoppered* funnel (*a*), a pipette (*b*) is used instead of an ordinary delivery-tube, so that the water cannot be drawn into the flask.* As the solution becomes more concentrated the gas dissolves less readily, and finally the water is saturated under the given conditions and begins to fume, the solution cooling down again.

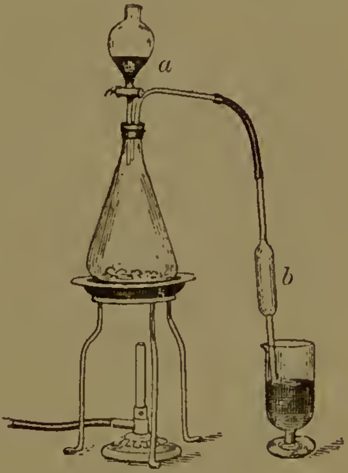

Fig. 55.

The *solubility* of the gas at 15° is very high (about 45,000), and a solution saturated at this temperature contains about 43 per cent. of hydrogen chloride and has a sp. gr. of 1·21. Such a solution is called *hydrochloric acid* or concentrated hydrochloric acid; if mixed with, say, two or more volumes of water it is called dilute hydrochloric acid.

When concentrated hydrochloric acid is heated *some* of the dissolved hydrogen chloride escapes and the solution becomes more dilute. This more dilute solution then evaporates or distils unchanged, leaving no residue; hence hydrochloric acid is *volatile.*

Hydrochloric acid has a sharp, sour taste; it burns or irritates the skin, turns blue litmus red, and attacks or corrodes many metals. These are properties which are shown by many substances, namely, those which are classed together as 'acids' (p. 248). When zinc, iron, or magnesium is placed in hydrochloric acid, the metal dissolves chemically and hydrogen is rapidly evolved; but lead is only attacked very slowly even on heating, and silver is not acted on.

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* The gas is so soluble that the water may rise in the pipette, but if the end of the pipette dips only just below the surface of the water, air is drawn in before the bulb is filled.

The water contained in hydrochloric acid is not regarded as impurity, because the only convenient way of storing and using hydrogen chloride is in aqueous solution. The weight of the gas in any sample of the acid is very easily determined by methods to be described later, and the ordinary commercial acid (sp. gr. 1·16) contains about 33 per cent. of hydrogen chloride. The concentrated acid 'fumes' because the invisible gas which escapes from it attracts and condenses atmospheric moisture, and thus a mist, consisting of minute drops of hydrochloric acid, is formed.

Composition of Hydrogen Chloride.—When an element is obtained simply by decomposing one pure compound, it is clear that the element must have been present in that compound; thus when mercuric oxide is decomposed by heat into oxygen and mercury, it is known that both these elements were contained in the original substance. On the other hand, when two (or more) different compounds are brought together and an element is obtained, further investigation is required in order to find out from which compound the element has been liberated, unless of course the constituents of one of them, at least, are known (compare p. 101). Thus when manganese dioxide is treated with hydrochloric acid the question arises, has the chlorine come from the dioxide or from the acid?

Now chlorine can be obtained by treating hydrochloric acid with many other substances besides manganese dioxide. When hydrochloric acid is heated with red-lead, chlorine is evolved. Since red-lead is known to be a compound of lead and oxygen only, the chlorine must be a constituent of hydrogen chloride. Further, since hydrochloric acid is acted on by many metals, and hydrogen is then evolved, it may be concluded that hydrogen is also a constituent of hydrogen chloride (compare footnote *, p. 146).

Now just as hydrogen oxide (water) is formed by burning hydrogen in oxygen, so hydrogen chloride may be produced by burning hydrogen in chlorine. A jet of hydrogen burning in the air continues to burn when it is plunged into a jar of chlorine, because the two gases combine. Fumes are seen, and the colour of the chlorine gradually disappears. When the contents of the jar are then shaken with a little water the fumes dissolve, and it can be proved that the solution contains hydrogen chloride. The synthesis of hydrogen chloride has also been accomplished in a previous experiment. When a candle 'burns' in chlorine, the materials contained in the wax or tallow are decomposed, the carbon separates as 'soot,' and the hydrogen combines with the chlorine, forming hydrogen chloride; if the jar is then covered with a glass plate and left for some time until the soot has settled, the fumes of hydrochloric acid are visible on removing the plate, and the presence of hydrogen chloride can be proved. The 'burning' of the candle is the combination of the hydrogen of the wax or tallow (p. 127) and the chlorine.

Evidence in support of this statement is obtained by pouring a little hot turpentine on to some filter-paper, which is then plunged into a jar of chlorine; spontaneous combustion occurs and a flame is seen, together with dense black smoke (soot), which gradually settles; on the jar being then uncovered, colourless fumes are produced, due to the hydrogen chloride coming into contact with atmospheric moisture. Since oil of turpentine is a compound of hydrogen and carbon only (p. 125), and the carbon separates as soot, the combustion is due to the union of the hydrogen and the chlorine.

Some Common Types of Chemical Change.—When a metal dissolves chemically in hydrochloric acid, hydrogen escapes as a gas, and when the solution is evaporated to dryness there remains a substance which is soluble in water. It can be proved that the weight of this residue is very much greater than that of the original metal, so that the other constituent of the hydrogen chloride, namely, the element chlorine, has combined with the metal, forming a *chloride.** It may be said, therefore, that the metal has *displaced*, or has been *substituted* for, the hydrogen of the acid.

This type of change, the displacement of one element in a compound by another, is very common, and is known as *substitution.*

Some metals—lead, for example—are only slowly acted on by hydrochloric acid, and others, such as mercury and copper, are not acted on appreciably. The *oxides* of all these metals, however, dissolve chemically in the acid, especially on warming, although they are insoluble in water. Thus when black copper oxide is heated with enough hydrochloric acid it gives a clear blue solution, by the evaporation of which yellowish-brown crystals of copper chloride are obtained.†

Similarly litharge (lead oxide) gives long colourless 'needles' of lead chloride, and mercuric oxide colourless needles of mercuric chloride. These products are identical with those formed by heating the respective metals in chlorine, and therefore they are *chlorides.*‡ No hydrogen is evolved when the oxides are treated with the acid. The chlorine of the hydrogen chloride combines with the metal, but what becomes of the hydrogen?

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* The presence of combined chlorine in this residue may be proved by the test described later (p. 150). As it is known that hydrochloric acid is an aqueous solution of hydrogen chloride (a gas composed of hydrogen and chlorine), and that when hydrochloric acid acts on a metal the latter is converted into its chloride, it may be concluded that the evolved hydrogen is liberated from the hydrogen chloride and *not* from the water. When a metal such as iron liberates hydrogen from water (p. 106), the metal is converted into its oxide.

† The change in colour from blue to yellowish-brown is due to the separation of combined water. Anhydrous yellow copper chloride, like anhydrous colourless copper sulphate (p. 36), gives a blue solution.

‡ The chloride obtained by treating a metal or the oxide of the metal with hydrochloric acid is *not* always identical with the chloride formed by the direct combination of the metal with chlorine. Some metals form two (or more) chlorides, and when they are placed in *excess* of chlorine the compound containing the larger proportion of chlorine is formed.

This question may be answered by passing hydrogen chloride slowly over a long layer of *dry* copper oxide or lead oxide, heated gently in a glass tube; a liquid condenses in the cold part of the tube, and it can be proved that this liquid is *water*. The hydrogen of the hydrogen chloride combines with the oxygen of the metallic oxide. When quicklime is treated in this way calcium chloride (p. 148) is formed, together with water. Therefore quicklime contains combined oxygen; it is the oxide of a metal, *calcium*.

The changes which occur when the oxide of a metal is treated with hydrochloric acid are examples of another common type of change called *double decomposition;* each of the original compounds is decomposed by the other, two (and only two) new compounds being formed, thus

$$\begin{array}{c}\text{copper}\\ \text{oxide}\end{array} + \begin{array}{c}\text{hydrogen}\\ \text{chloride}\end{array} = \begin{array}{c}\text{copper}\\ \text{chloride}\end{array} + \begin{array}{c}\text{hydrogen}\\ \text{oxide}\end{array}\ \text{(water).}$$

Experiments prove that in all such double decompositions the weight of the hydrogen and the weight of the chlorine contained in a given weight of hydrogen chloride are *exactly* sufficient to combine with the oxygen and metal respectively of the metallic oxide. Further, when the two compounds are taken in certain fixed proportions they are both completely decomposed, and only water and metallic chloride are produced; if one of the original compounds is in excess of this fixed proportion the excess remains unchanged, but only the same two products are formed. These facts merit careful consideration, and are explained later (p. 176).

Salts of Hydrogen Chloride.—The compounds produced by displacing the hydrogen of the 'acid,' hydrogen chloride, by a metal belong to an important class of substances which are called *salts* (p. 253).

Sodium chloride, which occurs in nature in such large quantities (p. 35), may be prepared in the laboratory in many ways. It is formed when the metal sodium (p. 253) is heated in chlorine; also when sodium carbonate is placed in hydrochloric acid. In preparing sodium chloride by the last-mentioned method, hydrochloric acid is added to a solution of sodium carbonate until effervescence ceases; it is then known that all the sodium carbonate has been changed. The solution is now evaporated; water and the *excess* of hydrogen chloride pass away, and anhydrous crystals of sodium chloride remain.

Calcium chloride may be obtained by heating the metal calcium in chlorine, but it is far more conveniently prepared by treating limestone or some other variety of calcium carbonate with hydrochloric acid in slight excess (p. 208). The solution is *filtered* if necessary (compare p. 74) and concentrated; when it is cooled large colourless *hydrated* crystals of calcium chloride are obtained. When these are heated they give *anhydrous* calcium chloride, the very hygroscopic substance so much used in drying gases.

Barium chloride is a 'salt' composed of a metal, barium, and chlorine; it is readily soluble in water.

Silver chloride.—Silver is not acted on by hydrochloric acid, but when silver oxide (a black powder) is warmed with the acid, a white 'curdy' substance, which is insoluble in water, is formed. This substance may be separated by filtration, washed, and dried; when heated at a dull-red heat it melts, but does not decompose. The melted substance solidifies on cooling to a horn-like mass, and is *identical* with the compound obtained by heating silver in a stream of chlorine; therefore it is a compound of these two elements, and is called *silver chloride.*

Silver dissolves chemically in nitric acid, a brown gas is evolved, and on evaporating the solution a colourless crystalline 'salt,' *silver nitrate*, is obtained. Now when hydrochloric acid is added to a solution of silver nitrate, a white curdy solid is immediately precipitated; this substance is silver chloride. Therefore the silver contained in a combined form in silver oxide or in silver nitrate may combine with the chlorine of hydrogen chloride and *displace the hydrogen*;* for this reason, although silver chloride is insoluble in water and cannot be prepared by treating silver with hydrochloric acid, it is nevertheless classed as a *salt.*

When hydrochloric acid is added to a solution of silver nitrate and the liquid containing the precipitated silver chloride in suspension is boiled, the precipitate clots together and settles, and the liquid becomes clear; if then a drop more hydrochloric acid is added, more precipitate may or may not be formed. It all depends on how much acid has already been added, because a given weight of silver nitrate requires a fixed weight of hydrogen chloride to change it into silver chloride. If, when no further precipitate is formed (that is, when *excess* of hydrochloric acid is present), the solution is filtered and evaporated to dryness on a water-bath, there is *no residue.* This fact proves (*a*) that silver chloride is insoluble in the liquid (which is a very dilute solution of volatile hydrochloric and nitric acids); (*b*) that the filtrate contains no silver nitrate (because this substance is known to be non-volatile).

With excess of hydrogen chloride, then, the *whole* of the combined silver in the silver nitrate is precipitated as silver chloride, because silver chloride is insoluble in the liquid present. For exactly the same reason the *whole* of the combined *chlorine* in hydrogen chloride is precipitated as silver chloride on adding *excess* of silver nitrate to a solution of hydrogen chloride.

This is an important general principle on which many qualitative and quantitative analyses are based: when two substances act on one another in a given solution forming a new substance which is insoluble in the liquid present, the whole of either of the original substances is decomposed on adding *excess* of the other; if the two substances are present in exactly the right proportion *both* are completely decomposed.

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* Hydrogen is not liberated as gas; a double decomposition occurs and water or nitric acid is formed (pp. 253 and 241).

A solution of silver nitrate may thus be used as a very delicate or sensitive 'test' for hydrogen chloride, since the formation of silver chloride is easily *seen*, and the compound is easily identified. A solution of silver nitrate also gives a precipitate of silver chloride when it is added to a solution of any other chloride such as sodium chloride (common salt), calcium chloride, barium chloride, and so on. The colourless crystalline substance (potassium chloride) which is formed together with oxygen when potassium chlorate is heated (p. 82) also gives with silver nitrate a precipitate of silver chloride; potassium chlorate does not give such a precipitate in spite of the fact that it contains combined chlorine, because it is not a chloride. The presence of *chlorides* in most natural waters is also proved by testing with silver nitrate, after concentrating the water if necessary.

The *percentage composition of silver chloride* was determined by various methods with very great care by Stas (1860), and as examples of his results the following may be given: 91·462 g. of silver were converted into silver chloride by heating the metal in chlorine; 121·4993 g. of silver chloride were obtained; the percentage composition, therefore, is, silver 75·28, chlorine 24·72. 108·549 g. of silver were dissolved in nitric acid, and the silver was precipitated as chloride with hydrochloric acid; 144·207 g. of silver chloride were obtained; the percentage composition, therefore, is, silver 75·27, chlorine 24·73.

All the substances used in these experiments were purified with the greatest care, and every other precaution was taken to reduce experimental error as far as possible. The results afford a striking confirmation of the law of fixed and definite proportions.

Percentage Composition of Hydrogen Chloride.—The composition of silver chloride being known, that of hydrogen chloride may be determined in the following manner: A small flask containing *distilled* water and fitted up as shown (fig. 56) is carefully weighed.

The lower end of the inlet-tube (*a*) is drawn out to lessen the bore, the upper one being closed with a piece of rubber tubing and glass rod; the end of the outlet-tube is similarly closed, but a slit is made in the rubber tubing at (*b*), so that if there is any pressure in the flask the slit is forced open and air escapes.*

The stopper of the inlet-tube (*a*) having been removed, this tube (*a*) is connected with an apparatus generating pure (dry) hydrogen chloride, which rapidly dissolves in the distilled water. After some time, and before the solution becomes saturated, the inlet-tube is disconnected, closed with its stopper as before, and the whole apparatus weighed again; the increase in weight gives the *weight* of hydrogen chloride in the solution. The contents of the flask are now carefully washed into a beaker, and there treated with excess of silver nitrate; the precipitated silver chloride is separated, washed, dried, and weighed.

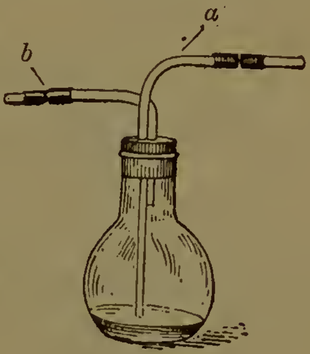

Fig. 56.

The calculation of the results is indicated by the following example:

Weight of hydrogen chloride dissolved, 2·3005 g.
" " silver chloride obtained, 9·046 g.
" " chlorine in the silver chloride $= \dfrac{9{\cdot}046 \times 24{\cdot}73}{100}$ $= 2{\cdot}237$ g.
" " hydrogen in the hydrogen chloride, $2{\cdot}3005 - 2{\cdot}237 = 0{\cdot}0635$ g.

The percentage composition of hydrogen chloride is thus found to be, hydrogen 2·76, chlorine 97·24.

There are other and more accurate methods by which the composition of hydrogen chloride has been determined.

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* This arrangement is known as a Bunsen-valve.

The chlorides of most of the metals are soluble in water, but silver chloride, as shown above, is insoluble and lead chloride only sparingly soluble in cold water. The percentage of chlorine (and therefore also the percentage of metal) in any soluble metallic chloride may be determined by dissolving a known weight of the chloride in (distilled) water, precipitating with excess of silver nitrate, and weighing the silver chloride thus produced.

CHAPTER XVIII.

The Properties of Gases and Vapours.

The terms solid, liquid, and gas are so well known that they have been used without explanation; it is now desirable to note the principal differences between these three *states* of matter, and to consider more particularly the general behaviour of gases and vapours.

A *solid* has a particular shape, which is not permanently altered except by a definite force, and even when its shape is altered its bulk or *volume* is not changed appreciably. The particles of a solid are generally arranged in definite crystalline forms. When a solid is heated it usually expands a little, and as the temperature rises it may pass into the liquid or gaseous state, or it may decompose.

A *liquid* has no particular shape; it adapts itself to any vessel in which it is placed; its particles move freely over one another and yield to the least pressure, but its *volume* is altered very little when the pressure on it is increased. When a liquid is heated it usually expands a little, and as the temperature rises or the pressure is diminished it may boil and pass into the gaseous state, or it may decompose.

A *gas* or *vapour* has no particular shape, but, as shown below, fills any vessel, however large, in which it is contained.

Its *volume* is greatly altered when the pressure on it, or its temperature, is changed. It is in these two respects particularly that gases and vapours may now be studied, although the matter really belongs to the science of physics.

Relation between the Volume and the Pressure of a Gas.—The graduated tube (*a*, fig. 57, I.) is filled with mercury by raising the reservoir (*c*) and opening the tap (*b*) until the liquid rises to (*b*); the tap (*b*) is then closed, the reservoir (*c*) is lowered again to the table-level, and dry hydrogen is passed through the side-tube (*d*) into the graduated tube (*a*) until the latter is about one-third filled; the side-tube (*d*) is then closed. The reservoir (*c*) is now raised by the side of (*a*) until the levels of the mercury are the same—that is to say, until the pressure is the same on both. The hydrogen is now under atmospheric pressure, say, 760 mm.; let its volume be, say, 35 c.c. The reservoir (*c*) is now raised (fig. 57, II.), where-

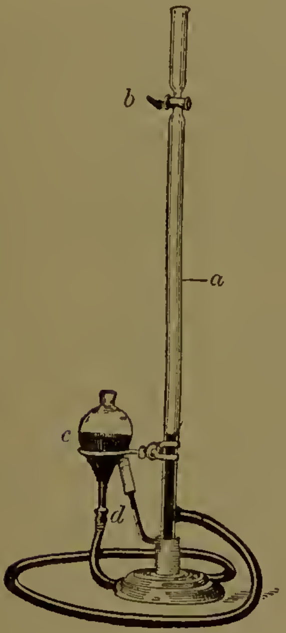

Fig. 57, I.

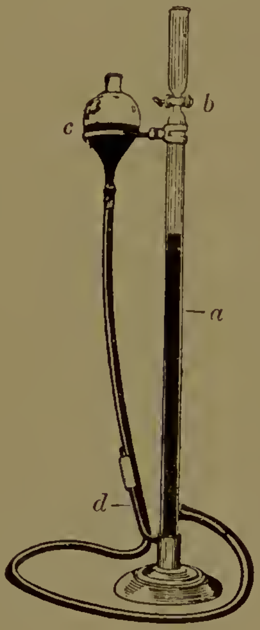

Fig. 57, II.

upon the volume of the gas in (*a*) diminishes; the height of the mercury-level in (*c*) above that in (*a*) is a measure of the *extra* pressure which has been put on the gas. Suppose this is 240 mm., then the *total* pressure is $760 + 240 = 1000$ mm. The volume is now 26·6 c.c.

Again raise the reservoir (*c*); the volume of the gas again diminishes. Let the extra pressure (difference in levels) now be 640 mm.; then the total pressure is $760 + 640 = 1400$ mm. The volume is now 19 c.c.

Finally, let (*c*) be raised until the extra pressure is 760 mm.; the total pressure is now 760×2 mm. The volume is now 17·5 c.c.

By doubling the original pressure the original volume is halved.

Let (*c*) be lowered again until the levels are the same; the pressure is now 760 mm. The volume is 35 c.c. By halving the pressure the volume is doubled.

Let (*c*) be lowered again until the mercury-level is 380 mm. below that in (*a*); the pressure is now $760 - 380 = \frac{760}{2}$. The volume is 70 c.c. By again halving the pressure the volume is again doubled; or by reducing the pressure from 760×2 mm. to 380 mm.—that is to say, to one-*fourth*—the volume is increased fourfold.

If, instead of hydrogen, oxygen or carbon dioxide is introduced into the tube, the results are exactly the same; further, if air, which is a mixture of oxygen, nitrogen, carbon dioxide, and other gases, is examined instead, or in fact any other gas or gaseous mixture, the results are the same. All gases are equally changed in volume by equal changes in pressure.

The relation between the volume and pressure of a gas was established by Boyle (1662), and is expressed by **Boyle's law**: '*When the temperature remains constant, the volume of a fixed mass of gas varies inversely as its pressure.*'

If the volume $(v) = 1$, under a pressure $(P) = 1$, then if P becomes 2, 3, 4, &c., v becomes $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, &c.; if P becomes $\frac{1}{2}$,

$\frac{1}{3}$, $\frac{1}{4}$, &c., the volume becomes 2, 3, 4, &c. $P \times v$ is always the same (a constant).

Thus in the above experiments

P = 760 mm.	v = 35 c.c.	Pv = 26600
P = 1000 "	v = 26·6 "	Pv = "
P = 1400 "	v = 19·0 "	Pv = "
P = 1520 "	v = 17·5 "	Pv = "
P = 380 "	v = 70·0 "	Pv = "

Since the volume of a gas varies so greatly with the pressure, it is obvious that if a globe or other vessel is filled with a gas, the *weight* of the given volume of gas varies with the pressure to which the gas was exposed when the vessel was filled. Suppose, for example, that the globe (fig. 23, p. 68) is filled with carbon dioxide, by passing a stream of gas through it, and the taps are closed when the barometer stands at 760 mm.; then if the experiment is repeated when the barometer happens to stand at 740 mm., a smaller *weight* of gas will be contained in the globe, because the gas is denser (more compressed) under the higher pressure. In weighing a known volume of gas, therefore, the pressure must be noted, otherwise the results of different experiments could not be compared. Now the weight of unit volume of a gas is usually given for a pressure of 760 mm. (one atmosphere), and when a gas is actually weighed under other pressures the result is reduced to this standard pressure.

Example.—A litre of hydrogen under a pressure of 735 mm. is found to weigh 0·0870 g. What would be the weight of a litre at 760 mm. (the temperature remaining constant)?

As the volume of a given weight of gas varies inversely as the pressure, the *volume* under 760 mm. pressure would be $\frac{1 \times 735}{760}$ litre; as this volume of gas weighs 0·0870 g., 1 litre of it under the same conditions would weigh $0{\cdot}0870 \times \frac{760}{735} = 0{\cdot}0899$ g.

Since a gas expands when the pressure on it is reduced (gases are *elastic*), if a single bubble of any gas is passed up into the Torricellian vacuum (footnote, p. 17) the gas at once expands and *fills* the vacuum; nay, more, it depresses the mercury in the tube until the final volume of the gas is to its original volume as the original pressure P (760 mm.) is to the final pressure P_1. Suppose that it *depresses* the mercury 12·66 mm.; it is now under a pressure (P_1) of 12·66 mm. Let the volume of the original bubble be 0·5 c.c.; its volume is now 30 c.c. ($0·5 \times 760 = 30 \times 12·66$).

If, instead of a bubble of a gas, a few drops of *water* are passed up into the vacuum, some of the water evaporates, and its *vapour* not only fills the vacuum but depresses the mercury. When the space becomes *saturated* with aqueous vapour, the amount by which the mercury is depressed, expressed in mm., is termed the *tension* of aqueous vapour. This tension (T) depends on the temperature t°, and a few values of T are given below;* at 100°, the boiling-point of water, T = 760 mm. (compare p. 19).

Other vapours behave in a similar manner.

When water is passed up into a *dry* gas, such as hydrogen, confined over mercury, the water evaporates in the gas, just as it does in a vacuum, until the gas is saturated with aqueous vapour. Thus in the above experiment, in which the mercury is depressed 12·66 mm. by *dry* gas, if water is then passed up, the mercury is further depressed by an amount corresponding with the tension of aqueous vapour at the temperature of the experiment. Consequently when a gas is saturated with aqueous vapour, its true volume is *increased* by the volume of the aqueous vapour present.

Now the total *observed* volume of the moist gas is partly that of the gas itself and partly that of the aqueous vapour, and the volume occupied by each is proportional to the *partial pressure* exerted (or supported) by it; hence

$$\frac{\text{true volume of gas}}{\text{total (observed) volume}} = \frac{\text{partial pressure of gas}}{\text{total pressure}}.$$

* t° . . .	0°	5°	10°	15°	20°
T in mm. .	4·5	6·5	9·2	12·7	17·4

In order, therefore, to obtain the volume of the dry gas, the tension of aqueous vapour at the particular temperature must first be subtracted from the *observed* pressure,* and the (true) partial pressure is then used in calculating the volume at standard pressure.

Example.—A graduated tube contains hydrogen at 5° saturated with aqueous vapour; the observed volume is 50 c.c. and the observed pressure 720 mm.* What would be the volume of the dry gas at 760 mm.?

At 5°, T=6·5 mm.; 720 − 6·5=713·5. The corrected volume, therefore, is $\frac{50 \times 713{\cdot}5}{760}$ c.c.

Relation between the Volume and the Temperature of a Gas.—The graduated glass tube (*a*, fig. 58), about 2 mm. in internal diameter, is sealed at the *lower* end; it contains dry hydrogen confined by the short column of mercury (*b*), which is so adjusted that when the temperature of the hydrogen is 15° the *volume* of the confined gas is 288 units. The tube (*a*) is fitted as shown in the wider tube (*c*), which also contains a thermometer (*d*).

Ice-cold water, containing melting ice, is now passed through the tube (*c*) from the inlet (*e*) until it overflows from the outlet (*f*). The hydrogen contracts, and when it has thus been cooled to 0° its volume becomes 273 units.

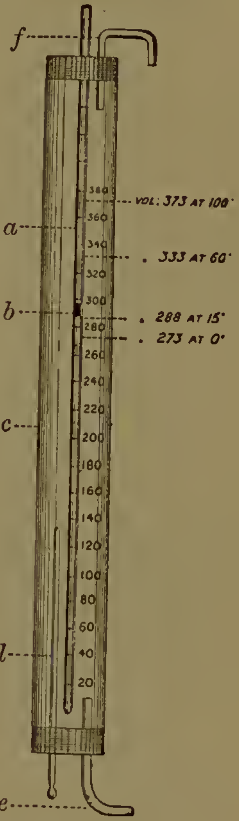

Fig. 58.

The ice-cold water is now run out and warm water is introduced, until the temperature of the hydrogen is, say, 60°; the volume of the gas is now 333 units.

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* The observed pressure is obtained by subtracting the length of the mercury column in the tube above the level of the mercury in the trough (the difference in level) from the height of the barometer at the time of the observation.

Finally all the water is run out and steam is passed through the tube (*c*); when the temperature of the gas reaches 100° the volume is 373 units.

Hence a *volume* of gas represented by

273 units at 0° becomes $288 = 273 + 15$ units at 15°
" " " " $333 = 273 + 60$ " 60°
" " " " $373 = 273 + 100$ " 100°

and for any intermediate temperature, t, the volume is $273 + t$ or $273\left(1 + \frac{t}{273}\right)$; in other words, 273 volumes at 0° increase by one volume for every increase in temperature of 1° C.; the increase per degree is $\frac{1}{273}$ of the volume at 0° C. On the gas cooling through any interval of temperature, the contraction is exactly the same as the expansion which occurred between those limits of temperature.

If, instead of dry hydrogen, oxygen or air or any other gas or mixture of gases is examined in a similar manner, the results are exactly the same. *Equal volumes of all gases expand equally for equal rises of temperature*, the pressure remaining constant. This general conclusion, established by Charles, Dalton, and Gay-Lussac, is generally known as **Gay-Lussac's or Charles' law.**

Absolute Temperature.—A gas at 0° contracts $\frac{1}{273}$ of its volume at 0° for every fall of 1°. 273 c.c. at 0° become 272 c.c. at $-1°$, 270 c.c. at $-3°$, 250 c.c. at $-23°$, and so on, until at $-273°$, *if* the gas continued to contract at the same rate, it would not have any volume. This temperature, $-273°$, is called the *absolute zero*, and if this point is used as the zero in expressing temperatures, the values are termed absolute temperatures; thus a temperature of $-20°$ on the Centigrade is $+253°$ on the absolute scale, 0° C. $= +273°$ absolute, 10° C. $= +283°$ absolute, and so on. The relation between the volume and temperature of a gas, therefore, may be stated as follows: *The volume of a gas is directly proportional to its absolute temperature*, the pressure being constant.

Since the volume of a gas varies so greatly with a change in its temperature, it is clear that if a glass globe is filled with a gas, say, at 20°, the *weight* of the gas is less than if the globe had been filled at 0°, the pressure being constant. In weighing a gas, therefore, its temperature, as well as its pressure, must be noted.

The weight of unit volume of a gas is usually given for 0°, so that if it is weighed at any other temperature the result must be reduced to the standard temperature.

Example.—A litre of hydrogen at 15° (and 760 mm.) weighs 0·08496 g.; what would be the weight of a litre of hydrogen at 0° (and 760 mm.)?

As the volume at 15° is to the volume at 0° as 288 : 273, the gas if cooled to 0° would only occupy $\frac{1 \times 273}{288}$ litre; as this volume weighs 0·08496 g., a litre at 0° would weigh $0{\cdot}08496 \times \frac{288}{273} = 0{\cdot}09$ g.

Under whatever known conditions a gas is measured (or weighed), it is possible to calculate what its volume (or weight) would be under any other conditions. As already stated, the results are generally given for a standard or Normal Temperature of 0° and a Normal Pressure of 760 mm., referred to by the letters N.T.P.

THE DETERMINATION OF THE DENSITY OF A GAS OR VAPOUR.

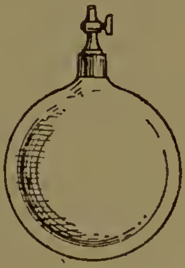

Fig. 59.

The determination of the weight of a given volume of gas requires special apparatus, and is by no means an easy task; a rough idea of the method, however, may be given.

The volume of a globe such as that shown in fig. 59 is first carefully determined. (How?) The globe is then weighed full of *dry* air, the temperature and pressure being noted. The air in the globe is then pumped out and the *loss* in weight is ascertained. From these data the weight of a litre (standard volume) of air at N.T.P. may be calculated.

As the globe displaces a large volume of air, its weight varies according to the temperature and pressure of the air it thus displaces. Therefore a similar globe is suspended from the other arm of the balance, and thus this source of error is avoided. As the two globes are *equally* affected, the observed loss in weight on pumping the air out of one of them is the true weight of the known volume of air under the known conditions.

Example.—Volume of globe, 1140 c.c. Loss in weight, 1·3602 g. t = 15°. Bar. = 740 mm.

The volume of the air at N.T.P. would be $1140 \times \frac{273}{288} \times \frac{740}{760}$ = 1052·2 c.c. Since this volume weighs 1·3602 g., 1 litre weighs $\frac{1{\cdot}3602 \times 1000}{1052{\cdot}2} = 1{\cdot}293$ g.

By first filling the globe with dry hydrogen, oxygen, or other gas, and then proceeding as before, the weight of a litre of the gas may be determined. The weight of a litre of hydrogen at N.T.P. is 0·09 g. (more exactly 0·08987 g.); as hydrogen is the lightest of all gases, the weights of other gases or vapours are conveniently expressed in terms of that of an equal volume of hydrogen measured under the same conditions. This important *physical constant* of a gas is called its *density* (vapour density, specific gravity). Thus the density of oxygen is 16; that is to say, this gas is 16 times heavier than an equal volume of hydrogen under the same conditions.

The density of the *vapour* of a substance which is solid or liquid at ordinary temperatures may also be determined; thus the density of water vapour may be ascertained by placing sufficient water in the globe, and then immersing the globe, all but the tap, in a bath of oil, heated at, say, 130°. The water boils, its vapour soon expels all the air from the globe, and if at the moment when all the water has been changed into vapour (that is, when steam ceases to escape) the tap is closed, the globe is then filled with water vapour at 130° and atmospheric pressure; it is cooled, cleaned, and weighed; the weight of the vacuous globe being also known, the density of water vapour at N.T.P. may be calculated.

Example.—Weight of globe full of water vapour, less weight of empty globe $=0{\cdot}8122$ g. Volume, 1500 c.c. $t=130°$. Bar. $=750$ mm.

The volume at N.T.P. would be $1500\times\frac{273}{403}\times\frac{750}{760}=1002{\cdot}8$ c.c.

The weight of 1 litre, therefore, is $\frac{0{\cdot}8122\times1000}{1002{\cdot}8}=0{\cdot}81$ g.

The weight of 1 litre of water *vapour* at N.T.P. being 0·81 g., the *density* of water vapour is $\frac{0{\cdot}81}{0{\cdot}09}=9$.

It should be clearly understood that although the water vapour would of course condense if it were cooled to N.T.P., it is possible to calculate what its density would be, assuming that it did not liquefy; this is done in order that its density may be compared with those of other gases or vapours at N.T.P. If 100° and 50 mm. were fixed as the standard temperature and pressure respectively, the *relative* weights of equal volumes of hydrogen and water vapour would be 1 : 9, as before.

Other more convenient methods of determining the densities of vapours are known, but the principle is the same in all cases; that is to say, the weight and the volume of the vapour under known conditions are determined, and the weight of 1 litre is then compared with that of a litre of hydrogen under the same conditions.

In making experiments with gases two forms of apparatus are very often used. One of these (fig. 60) is a simple graduated tube, the eudiometer (p. 244), in which the gas is confined over mercury; for purposes described later, the tube is often provided with two platinum wires (a, a), fused into and passing through the glass, as shown. In order to ascertain the volume of the gas at N.T.P. from the *observed* volume, the temperature of the surrounding atmosphere is noted, and also the barometric pressure; the pressure on the gas is the barometric pressure *less* the difference in level (x, y;

footnote, p. 157). If the gas is wet, the tension of aqueous vapour (T) must be subtracted from the observed pressure (compare p. 156).

Example.—Observed volume of a wet gas $= 50{\cdot}2$ c.c. $t = 10°$. Difference in level, 325 mm. Bar. $= 750$ mm. T at $10° = 9{\cdot}2$ mm.

The true pressure, therefore, is $750 - 325 - 9{\cdot}2$ mm. Hence the volume at N.T.P. is $50{\cdot}2 \times \frac{415{\cdot}8}{760} \times \frac{273}{283}$ c.c.

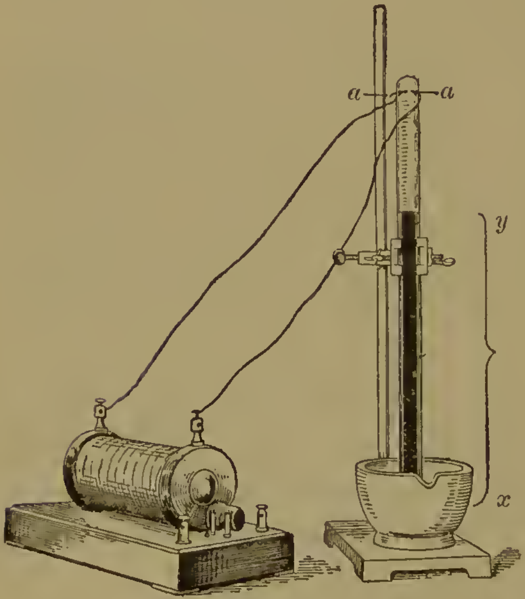

Fig. 60.

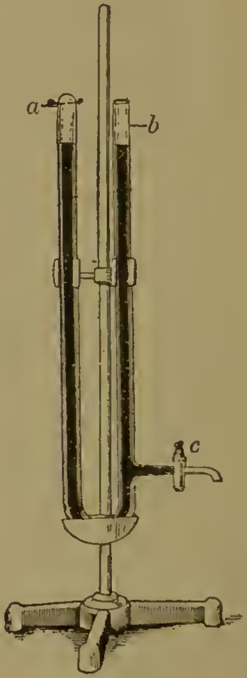

Fig. 61.

The other form of apparatus is shown in fig. 61, and is also provided (at *a*) with platinum wires. By pouring mercury into the open tube (*b*) or running it out from the tap (*c*) until the levels are the same in the two tubes, the gas may be brought to atmospheric pressure before and after any experiment; in such cases the true pressure on the gas is the barometric pressure at the time of the experiment, *less* the tension of aqueous vapour for the given temperature if the gas is wet.

Experiments have shown that all vapours and gases pass into the liquid state when they are cooled to a sufficiently low temperature, and if further cooled sufficiently they freeze, solidify, or crystallise.*

The temperatures at which different vapours and gases liquefy are widely different; thus at 760 mm. water vapour liquefies at 100°, ether vapour at 35°, chlorine at $-34°$, carbon dioxide at $-79°$, hydrogen chloride at $-84°$, oxygen at $-182·5°$, nitrogen at $-194°$, and hydrogen at $-252·5°$.†

A mixture of liquefied gases may be separated into its components by fractional distillation.

Some vapours and gases may be liquefied by pressure at ordinary temperatures; thus chlorine under 9 atmospheres, and carbon dioxide under 38·5 atmospheres, are condensed to liquids. It was shown by Andrews (1863), however, that for every gas there is a particular temperature above which it cannot be liquefied, however great the pressure; carbon dioxide, for example, cannot be liquefied above 30°. This temperature, above which liquefaction does not occur, is called the critical temperature of the gas, and the pressure required to liquefy it at its critical temperature is called the critical pressure of that gas.

The term gas may be restricted to that state of a substance in which it exists above its critical temperature, the state below its critical temperature being called vapour. The terms, however, are not always used in this sense, and that of vapour is generally employed when the same substance exists in a liquid state at ordinary temperatures and pressures.

Solubility of Gases.—The *weight* of a gas which is dissolved by a given weight of water (or other solvent) at a given temperature is directly proportional to the pressure (provided that the gas and the solvent do not *combine*). As, however, the volume of a gas is inversely proportional to the pressure, the *volume* of a given gas dissolved by a given weight (or volume) of water is constant, and independent of the pressure (**Henry's law**, 1803).

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* Compare footnote, p. 19.

† The laws of Boyle and Charles are not strictly true when a gas is at such a temperature and pressure that it is not far removed from its liquefying or boiling point. A *perfect* gas is an ideal or *imaginary* gas which would show under all conditions the behaviour expressed by these laws.

Thus the *solubility* of oxygen at 0° and 760° is 4·86; that is to say, 100 volumes of water dissolve 4·86 volumes of the gas. If the pressure is increased to 2 atmospheres, the same volume of oxygen gives a saturated solution; but the weight of the gas in this volume, and therefore in the solution, is twice as great as before.

Later on it was shown by Dalton that when a mixture of two gases is shaken with water at a given temperature, until the solution is saturated, the volume of each gas which is dissolved depends on (*a*) the solubility of the gas, (*b*) its pressure. Now in any gaseous mixture the pressure on any one component is directly proportional to its percentage by volume; each component shares the total pressure (or is under a *partial* pressure, p. 156) in proportion to its volume (Dalton's *Law of Partial Pressures*, 1805). Hence, when air, which is a mixture of 4 volumes of nitrogen and 1 volume of oxygen, is bubbled through water, say, at 15°, the relative volumes which are contained in the saturated solution are: oxygen, 3·36 × 1 (p. 85); nitrogen, 1·65 × 4 (p. 97); or, roughly, 1 : 2. If the solution is boiled and the expelled gases are collected and examined, it is found that such 'air' contains about 35 per cent. of oxygen. It is thus possible to effect a partial separation of the components of the atmosphere by one operation of fractional solution, a fact which indicates that air is a mixture (compare p. 96).

Diffusion of Gases.—When a gas-jar containing hydrogen and closed with a glass plate is inverted and placed on a similar jar containing carbon dioxide, then, on the glass plates being removed and the two jars fitted together, the hydrogen immediately begins to pass *downwards* and the carbon dioxide *upwards*. If after about two minutes the jars are separated, it can be shown that they both contain a mixture of the two gases. The contents of both jars take fire on applying a lighted taper, proving the presence of hydrogen; and if tested with lime-water, both vessels are found to contain carbon dioxide. Although carbon dioxide is twenty-two times heavier than hydrogen the two gases have mixed, and, if left long enough, the mixture becomes perfectly homogeneous; that is, it contains the same proportion of the two gases in every part.

This movement or passage of a gas from one vessel to another also takes place even if the vessels are separated by some *porous* material, such as unglazed earthenware or plaster of Paris, as shown by the following experiments.

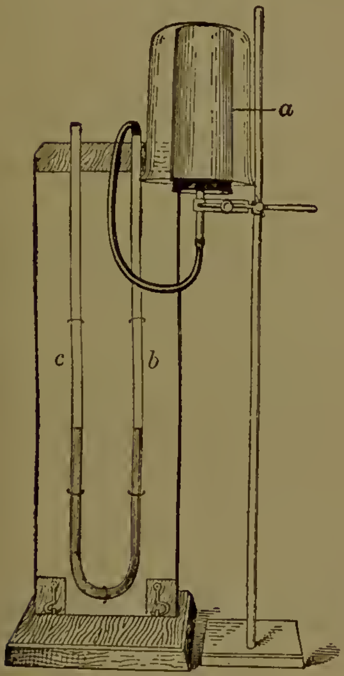

Fig. 62, I.

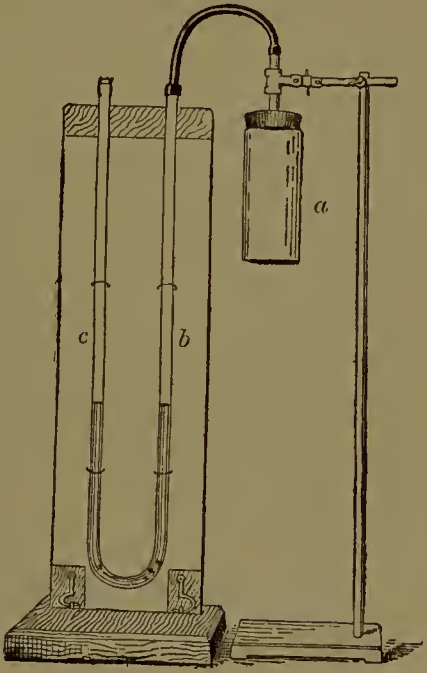

Fig. 62, II.

The earthenware jar (*a*, fig. 62, I.), filled with air at atmospheric pressure, is closed with a rubber bung, through which passes a glass tube connected with the U-tube containing a little (coloured) water. A large beaker filled with hydrogen is inverted over the jar; it is then seen by the movement of the water-gauge that the pressure in the jar (*a*) almost immediately becomes *greater* than one atmosphere. If when the water-level in (*b*) ceases to be depressed the beaker is removed, the water slowly rises in (*b*) until it is higher than in (*c*), proving that the pressure in the jar is now *less* than one atmosphere; the water in (*b*) then slowly falls, and the levels finally become the same.

This experiment shows that hydrogen passes or *diffuses* through the porous walls into the jar faster than the air passes out, thus causing an increased pressure. When the jar has become filled with a mixture of hydrogen and air, and the beaker is then removed, the hydrogen passes out more quickly than the air passes in, and the pressure is thus reduced below that of one atmosphere.

The earthenware jar (*a*, fig. 62, II.) of the similar piece of apparatus contains air under atmospheric pressure. When it is surrounded by a beaker filled with carbon dioxide the level of the water in (*b*) rises, proving that the air has passed outwards more quickly than the carbon dioxide has passed inwards; if when the pressure in the jar ceases to diminish the beaker is removed, the water falls in (*b*) until its level is below that in (*c*), proving that the air is passing into the jar more quickly than the carbon dioxide passes out.

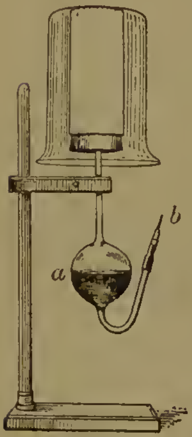

Fig. 63.

The fact that hydrogen diffuses more rapidly than air may also be proved with the aid of the apparatus shown in fig. 63, in which the porous earthenware jar (containing air) is connected with the bulb-tube (*a*), which contains coloured water. On a beaker filled with hydrogen being inverted over the earthenware jar a fine jet of water is forced out of the nozzle (*b*).

It must, therefore, be concluded that a light gas passes or *diffuses* through a porous material more rapidly than a heavy gas; that is to say, a larger *volume* of the light gas diffuses in a *given time*.

Graham's Law.—The results of quantitative experiments carried out by Graham (1831) showed that '*the rate of diffusion is inversely proportional to the square root of the density of the gas;*' thus the relative rates of diffusion of hydrogen, oxygen, and carbon dioxide are $\frac{1}{\sqrt{1}} : \frac{1}{\sqrt{16}} : \frac{1}{\sqrt{22}}$; that is to say, these values show the relative volumes of the gases which would pass through a given porous area in the *same* time under the same conditions.

A piece of apparatus similar to that shown in fig. 57, II. (p. 153) may be used to study the rate of diffusion of gases. The graduated tube (a), which contains the gas confined over mercury, is provided with a tap (b), the opening of which is closed with a platinum plate pierced with an extremely small hole. On the tap being opened the pressure of the mercury in (c) causes the gas to escape sufficiently rapidly to prevent air from diffusing into the tube. The *time* required for the escape of a fixed volume of different gases under a fixed pressure may thus be determined, and it is found that the *time* is directly proportional (the *velocity* inversely proportional) to the square root of the density of the gas.

If a mixture of equal volumes of oxygen and nitrogen is passed slowly through the unglazed earthenware tube (a, fig. 64), and the air in the surrounding glass tube is removed by connecting (b) with a pump, the gaseous mixture which diffuses through the earthenware tube would consist of nitrogen and oxygen in the proportion $\frac{1}{\sqrt{14}} : \frac{1}{\sqrt{16}} = 52 : 48$ (approximately) by volume; a *partial* separation of the gases has thus been accomplished. If air is diffused in the same way, then, as the relative volumes of the nitrogen and oxygen are originally 4 : 1 approximately, the partial pressures on the two gases are also in this proportion (p. 164); consequently, as the rate of diffusion varies directly as the pressure, the *diffused* gas would consist of nitrogen

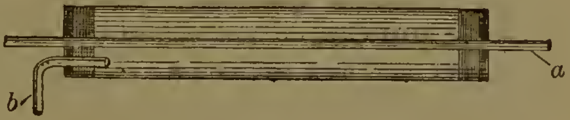

Fig. 64.

and oxygen in the proportion $4 \times \frac{1}{\sqrt{14}} : 1 \times \frac{1}{\sqrt{16}}$ by volume, and would therefore contain a larger proportion of nitrogen than does 'the air.' The fact that the two principal gases of the atmosphere may be partially separated in this way is further evidence that they are not combined.

The process of diffusion is sometimes used to effect a partial separation of the components of a gaseous mixture. It may also be employed to determine the density of a gas by finding the rate of diffusion with the apparatus described above, and comparing the result with that obtained with a gas of known density.

Example.—A certain volume of a gas diffuses in 9·4 minutes; the same volume of hydrogen diffuses in 2 minutes. The *times* are 4·7 : 1, and the densities $(4{\cdot}7)^2 : 1^2 = 22 : 1$.

Kinetic Theory of Gases.—When a solid substance passes into a liquid the change in volume is relatively small, but when a solid or liquid is transformed into a gas or vapour the increase in volume is relatively very great; the gas or vapour is very attenuated; it is highly compressible, or, in other words, its volume is greatly diminished by pressure.

These facts seem to show that the actual matter of which a gas consists is *not continuous;* that is to say, the space occupied by the gas is not filled by matter, and it may be supposed that a gas is composed of extremely small, solid *particles* of matter, separated from one another by distances which are large in comparison with the particles themselves. As these particles do not collect or 'settle' at the bottom of any vessel, and as a gas rapidly escapes from any open vessel in which it is placed, and diffuses through porous substances, it must be supposed that the particles of a gas are in constant *motion.* This supposition makes it necessary to assume further that the particles are *perfectly elastic;* otherwise, by colliding with one another and banging against the walls of the containing vessel, they would finally come to rest. It may then be further assumed that the constant bombardment of the walls of the containing vessel by the extremely small, solid particles moving with great velocity produces the *pressure* of the gas.

Now it can be shown that these speculations regarding the nature of gases and vapours agree with or account for all known facts relating to the gaseous state; for example, they are in agreement with the laws of Boyle, Charles, Henry, and Graham. Hence these speculations, originated by Bernoulli in 1738, and developed by Waterston, Clausius, Maxwell, and others, have become a highly important theory, known as the *kinetic theory of gases.*

CHAPTER XIX.

Equivalents—The Law of Multiple Proportions.

As hydrogen chloride, like every (pure) compound, has a fixed composition, it is obvious that when *any weight* of hydrogen chloride is decomposed, the *relative* weights of the hydrogen and chlorine obtained from it are also fixed and unchangeable. Now when hydrogen chloride is decomposed by a metal the hydrogen is set free, while the chlorine combines with the metal in fixed proportion to form a chloride; it follows, therefore, that a given weight of a given metal, with excess of hydrogen chloride, must give a fixed weight of hydrogen. But do all metals which act on hydrogen chloride displace the same or different weights of hydrogen? This question may be answered by the results of simple experiments.

A weighed piece of clean magnesium ribbon (say 0·0324 g.) bent into a V is pushed up (at *a*, fig. 65) into a burette, which is then completely filled with and inverted in a trough of water; hydrochloric acid is poured into the funnel (*b*), and by cautiously opening the tap for a *moment* most of the acid is allowed to flow into the burette without any air being admitted. The acid mingles with the water and soon reaches the magnesium; the hydrogen which is then evolved collects in the burette. When the *whole* of the metal has disappeared, the lower end of the burette, closed with the thumb, is plunged into a deep cylinder containing water, and the thumb is removed. The burette is then raised or lowered until the water-levels inside and outside are the same; the temperature of the water (gas) is noted, and also the height of the barometer. The data are now available for calculating the weight of hydrogen liberated by 1 g. of magnesium. 0·0324 g. of magnesium gives 32·7 c.c. of hydrogen measured *moist* at 16°; Bar. = 752 mm. Deducting T (p. 156), P = 752 – 13·5 = 738·5. The *volume* of the hydrogen at N.T.P., therefore, is $32{\cdot}7 \times \frac{273}{289} \times \frac{738{\cdot}5}{760} = 30{\cdot}0$ c.c. Since 1 litre of hydrogen weighs 0·09 g., the *weight* of 30 c.c. is 0·0027. Hence 1 g. of magnesium gives $\frac{0{\cdot}0027 \times 1}{0{\cdot}0324} = 0{\cdot}0833$ g. of hydrogen.

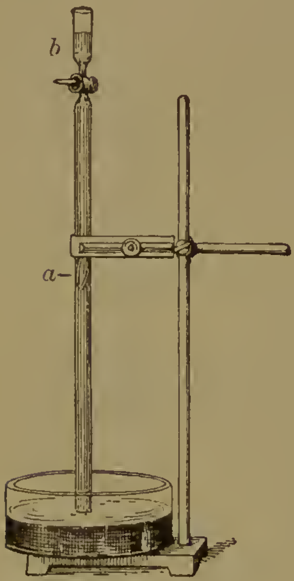

Fig. 65.

The weight of hydrogen liberated by a given weight of zinc may be determined in a similar manner. The weighed metal is placed in the centre of a trough and covered with a funnel, over which the burette filled with water is inverted. The acid is poured into the trough.

Another form of apparatus often used for measuring the volume of gas obtained in a chemical change is shown in fig. 66. This apparatus may be used in finding the weight of hydrogen liberated by a weighed quantity of a metal. The flask (*a*) contains a weighed quantity of zinc (say 0·9 g.), some water, and a small tube (*b*) containing concentrated hydrochloric acid; it is connected with the large bottle full of water, and from the latter passes a siphon, closed with a pinch-clamp (*c*) and filled with water, dipping into a graduated cylinder (*d*) containing a little water. When the apparatus is fitted up as shown, (*c*) is opened and the cylinder (*d*) is raised (in a slanting position) until the water-levels in (*d*) and in the large bottle are and remain the same; the moist air in (*a*) is now under atmospheric pressure, and the clamp (*c*) being *temporarily* closed, the volume of *the water in the cylinder is noted.* The tube (*b*) is now tipped on its side; the acid then acts on the zinc, and the liberated hydrogen drives water into (*d*).

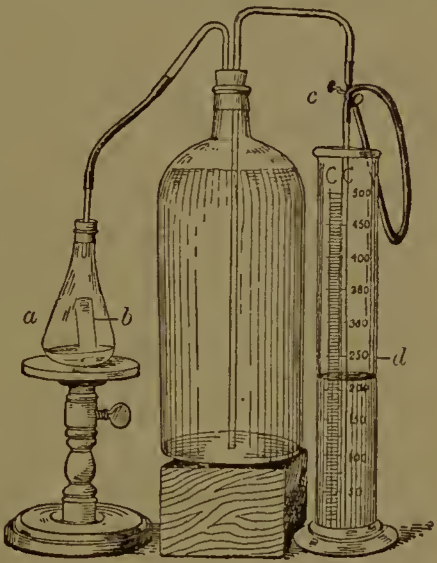

Fig. 66.

When the metal has disappeared and the apparatus has been left to cool if necessary, the water-levels are adjusted as before, so that the gas in (*a*) is at atmospheric pressure, and the volume of the water in (*d*) is again noted; also the temperature of the water (gas) and the height of the barometer. The volume of the liberated hydrogen is measured by subtracting the original volume of water in (*d*) from the final volume, as this is the volume of water which has been driven out by the gas.

Example.—0·9 g. of zinc. Volume of water expelled = volume of hydrogen = 337 c.c. $t = 16°$ (and $T = 13·5$ mm). Barometer = 752 mm. The volume of (dry) gas at N.T.P. would be $337 \times \frac{273}{289} \times \frac{752 - 13·5}{760} = 309$ c.c., which would weigh 0·0278 g.

Hence 1 g. of zinc liberates 0·0309 g. of hydrogen. In a similar manner it can be found that 1 g. of iron liberates 0·036 g. of hydrogen.

Now hydrogen is also liberated when the above metals are treated with dilute sulphuric acid (p. 223), and by quantitative experiments, carried out exactly as those described, it is found that a given weight of a metal always gives the same weight of hydrogen whether sulphuric acid or hydrochloric acid is used; the weight of the *displaced* hydrogen depends on the weight of the metal, which dissolves chemically and is independent of the nature of the acid.*

From the weight of the hydrogen liberated or displaced by 1 g. of each of the above metals, the weight of metal required to displace 1 g. of hydrogen from either of the acids may be calculated by simple proportion. The values thus obtained in accurate experiments are: magnesium 12·1, zinc 32·4, iron 27·8 g. The relative weights of these metals, expressed by the numbers 12·1, 32·4, and 27·8, are thus *equal* or *equivalent* in what may be called hydrogen-displacing value. Other common metals do not displace hydrogen from hydrochloric or sulphuric acid quickly at ordinary temperatures, and so it is impossible to find their equivalent weights directly by methods such as those described above. This, however, may be done indirectly.

Thus, although silver does not dissolve in hydrochloric acid, silver nitrate and hydrochloric acid give silver chloride (p. 148); in this change hydrogen is not liberated as gas, but that it is displaced from the hydrogen chloride is proved by the formation of silver chloride. Now, the composition of silver chloride being known (p. 150), and also that of hydrogen chloride (p. 151), the weight of silver required to displace

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* The *weight* of the hydrogen displaced by a known weight of a metal may also be determined by a method similar to that used in finding the weight of carbon dioxide which is obtained from a known weight of sodium carbonate (compare p. 77), but the experimental error is large.

1 g. of hydrogen from hydrogen chloride may be calculated and found to be 107·1 g.*

Since 2·76 g. of hydrogen combine with 97·24 g. of chlorine, 1 g. of hydrogen combines with $\frac{97{\cdot}24 \times 1}{2{\cdot}76} = 35{\cdot}2$ g. of chlorine.

Since 24·7 g. of chlorine combine with 75·3 g. of silver, 35·2 g. of chlorine combine with $\frac{75{\cdot}3 \times 35{\cdot}2}{24{\cdot}7} = 107{\cdot}1$ g. of silver.

As all metals combine with chlorine, the composition of any metallic chloride may be determined either by passing chlorine over a weighed quantity of the metal and weighing the product, or by the method already mentioned (p. 152). The composition of any chloride being known, the hydrogen-displacing power of the metal contained in it may be calculated, just as in the case of silver. Chloride of copper (cupric chloride), for example, has the composition, copper 47·3, chlorine 52·7 per cent.; hence the weight of copper which combines with 35·2 g. of chlorine is 31·5 g.*

By direct or indirect methods, such as those indicated, it is possible to assign to each of the metals a number which expresses the weight of that metal required to displace *one gram* of hydrogen; but since 1 g. of hydrogen combines with 35·2 g. of chlorine, the weight of any metal which displaces 1 g. of hydrogen from hydrogen chloride is *also* the weight of that metal which combines with 35·2 g. of chlorine.

Such values now begin to gain in importance, as they represent the relative weights of the metals which are equal or equivalent in *two* respects; is it possible to extend this idea of equivalent weights to other elements besides metals, hydrogen, and chlorine? Many metals combine directly with oxygen, and the composition of such oxides is often easily determined. The composition of a metallic oxide being known, it is easy to calculate the weight of oxygen which combines with the equivalent weight of the metal. Thus the composition of copper oxide is, copper 79·9, oxygen 20·1 per cent.; and that of magnesium oxide, magnesium 60·35, oxygen 39·65 per cent.; therefore 31·5 g. of copper combine with 7·94 g. of oxygen, and 12·1 g. of magnesium also combine with 7·94 g. of oxygen. From the known composition of the oxides of iron, zinc, and silver it is found that

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* The results given here and in the following pages may not be *exactly* those calculated from the data supplied, as the latter are often given only to 1 decimal place. If the most accurate experimental values are considered, then the results are as stated.

27·8 g. of iron combine with 7·94 g. of oxygen,
32·4 g. " zinc " " 7·94 g. "
107·1 g. " silver " " 7·94 g. "

These results may be now summarised as follows:

Weight of Element.		Weight of Hydrogen displaced by given Weight of Metal.	Weight of Chlorine with which given Weight of Metal Combines.	Weight of Oxygen with which given Weight of Metal Combines.
Magnesium	12·1 g.	1 g.	35·2 g.	7·94 g.
Zinc .	. 32·4 g.	1 g.	35·2 g.	7·94 g.
Copper	. 31·5 g.	1 g.	35·2 g.	7·94 g.
Iron .	. 27·8 g.	1 g.	35·2 g.	7·94 g.
Silver	. 107·1 g.	1 g.	35·2 g.	7·94 g.

Clearly these equivalent weights are of considerable importance, as they express the weights of the metals in grams which displace 1 g. of hydrogen, or combine with 35·2 g. of chlorine, or combine with 7·94 g. of oxygen. It is also evident that equivalent weights for the elements chlorine and oxygen have also been obtained, because the values 35·2 and 7·94 respectively are the relative weights of these elements which combine with one equivalent weight of any given metal. The values 1, 35·2, and 7·94 also express the relative weights of the elements hydrogen and chlorine, hydrogen and oxygen, which combine together, the composition of hydrogen chloride being, hydrogen = 1, chlorine = 35·2; and that of water (p. 110), hydrogen 11·19, oxygen 88·81 = 1 : 7·94.

By analysing compounds of other elements and then making simple calculations such as the above it is possible to assign to each element a number termed its *equivalent weight*, or simply its **equivalent** (E); this number expresses *the weight of the element in grams which combines with or displaces one gram of hydrogen.*

Although the numbers deduced above were obtained by taking unit weight of hydrogen as a basis, it is clear that any fixed weight of any other element might be taken as a standard instead without affecting the relationship and significance of the equivalents. Thus if 1 g. of oxygen served as basis, since 7·94 g. of oxygen are equivalent to 1 g. of hydrogen it would simply be necessary to divide the above numbers by 7·94; their *relative* values would not be changed. The equivalent of an element, therefore, is the weight of that element in grams which combines with or displaces a standard weight of some standard element.

The meaning of the term equivalent may perhaps be further illustrated by considering the results of experiments in which one metal directly displaces another. When iron is placed in a solution of copper sulphate, the iron dissolves chemically and copper is precipitated (p. 46); if a weighed quantity of clean iron wire (say 0·5 g.) is placed in a warm solution of *excess* of copper sulphate and left for some time, the wire disappears completely, and a reddish deposit of copper is obtained; this precipitate may be separated by filtration, washed, dried, and weighed. It is thus found that 0·5 g. of iron displaces 0·567 g. of copper, so that one equivalent of iron, namely, 27·8 g., displaces $\frac{27{\cdot}8 \times 0{\cdot}567}{0{\cdot}5} = 31{\cdot}5$ g. or one equivalent of copper.

Zinc displaces copper from copper sulphate under similar conditions, and experiments show that 32·4 g. (or one equivalent) of zinc displace 31·5 g. (or one equivalent) of copper.

Similarly magnesium displaces silver from a solution of silver nitrate, and it is found that 12·1 g. of magnesium precipitate 107·1 g. of silver.

In these experiments one metal is *substituted for* another; just as a metal may be substituted for the hydrogen of hydrogen chloride (p. 146), so also certain metals may be substituted for the copper in the compound copper sulphate, and so on.

Another excellent illustration of the meaning of the term equivalent is afforded by the change known as *double decomposition* (p. 147), as, for example, the interaction of copper oxide and hydrochloric acid. In each of these compounds the elements are combined in *equivalent* quantities: copper 31·5, oxygen 7·94; hydrogen 1, chlorine 35·2; this is also the case as regards the products copper chloride and water; hence double decomposition occurs without a particle of any one of the four elements being liberated.

Copper oxide	+	Hydrogen chloride	give	Copper chloride	+	Hydrogen oxide
Λ		Λ		Λ		Λ
{Copper, 31·5		Hydrogen, 1		Copper, 31·5		Hydrogen, 1
{Oxygen, 7·94		Chlorine, 35·2		Chlorine, 35·2		Oxygen, 7·94

It is also possible, as is indicated by this example, to extend the idea of equivalent weights to *compounds; the relative weights of any two compounds which undergo double decomposition are equivalent to one another.* Since, for example, 36·2 of hydrogen chloride enter into double decomposition with $12·1 + 7·94 = 20·04$ of magnesium oxide, or with $32·4 + 7·94 = 40·34$ of zinc oxide, these weights of the respective compounds are equivalent to 39·44 g. of copper oxide and to one another.

THE LAW OF MULTIPLE PROPORTIONS.

It follows from what has now been stated that the equivalent (E) of *any* element may be determined by finding the composition by weight of any compound which that element forms with any other element, provided that the equivalent of the latter is known. As the equivalent is thus based on the analysis of a compound of fixed composition, it is clear that the equivalent deduced from this analysis has also a constant value.

The equivalent of carbon, for example, may be calculated from the composition by weight of carbon dioxide (p. 116); since 27·27 g. of carbon combine with 72·73 g. of oxygen, the weight of carbon combined with 7·94 g. (one equivalent) of oxygen is $\frac{27{\cdot}27 \times 7{\cdot}94}{72{\cdot}73} = 2{\cdot}97$.

But, as already shown, carbon and oxygen also form a compound, carbon monoxide, which contains carbon 42·8 and oxygen 57·2 per cent. (p. 122); if now the equivalent of carbon is calculated from the composition of this compound the value obtained is $\frac{42{\cdot}8 \times 7{\cdot}94}{57{\cdot}2} = 5{\cdot}94$.

Hence carbon has two different equivalents, corresponding with its two oxides, the compositions of which are:*

$$\text{Carbon monoxide}\begin{cases}\text{Carbon, 6.}\\ \text{Oxygen, 8.}\end{cases} \qquad \text{Carbon dioxide}\begin{cases}\text{Carbon, 3.}\\ \text{Oxygen, 8.}\end{cases}$$

Many other cases are known in which two elements unite in different proportions by weight. The black copper oxide (*cupric* oxide), obtained by various methods (p. 46), and consisting of copper 79·9, oxygen 20·1 per cent. (p. 50), is not the only oxide of copper known; a red oxide (*cuprous* oxide) may also be prepared from copper sulphate and by other methods. This compound may be analysed quantitatively by heating a weighed quantity in a stream of dry hydrogen and weighing the copper and the water which are formed (p. 46); from the weight of the water, that of the oxygen may be calculated. The substance is thus proved to be an oxide of copper, and its composition is determined at the same time.

10 g. of the red oxide gave 1·26 g. of water and 8·88 g. of copper. The weight of oxygen in 1·26 g. of water is 1·12 g.; the composition of the oxide, therefore, is, copper 88·8, oxygen 11·2 per cent.

Now the equivalent of copper calculated from the composition of the black oxide is 31·5 (p. 174), and that calculated from the composition of the red oxide is $\frac{88\cdot8 \times 7\cdot94}{11\cdot2} = 63\cdot0$; hence copper has two different equivalents corresponding with its two oxides, the compositions of which are: *

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* The values are given in whole numbers for the sake of clearness.

$$\begin{array}{c}\text{Black oxide}\\ \text{(cupric)}\end{array}\left\{\begin{array}{l}\text{Copper, } 31\cdot5.\\ \text{Oxygen, } 8.\end{array}\right. \qquad \begin{array}{c}\text{Red oxide}\\ \text{(cuprous)}\end{array}\left\{\begin{array}{l}\text{Copper, } 63.\\ \text{Oxygen, } 8.\end{array}\right.$$

When red lead is placed in nitric acid it is decomposed; one of the products is a brown powder which is not further acted on by nitric acid. This powder may be separated by filtration, washed well, and dried. It is called *lead dioxide.*

When lead dioxide is heated, oxygen is liberated and litharge (p. 80) remains; 100 g. of lead dioxide lose 6·7 g. of oxygen and give 93·3 g. of litharge.

When litharge is heated in a stream of dry hydrogen, water is formed and lead remains; the composition of litharge may thus be determined (compare above), and found to be, lead 92·82, oxygen 7·18 per cent.

The composition of litharge being known, that of lead dioxide may be calculated as follows: Since 100 g. of litharge contain 92·82 g. of lead, 93·3 g. of litharge (the quantity obtained from 100 g. of lead dioxide) contain 86·6 g. of lead; the composition of lead dioxide, therefore, is, lead 86·6, and oxygen 13·4 per cent.

Now the equivalent of lead calculated from the composition of lead dioxide is 51·3, that from the composition of litharge 102·6; hence lead has two different equivalents corresponding with the two oxides, the compositions of which are: *

$$\text{Lead dioxide}\left\{\begin{array}{ll}\text{Lead,} & 51\cdot3.\\ \text{Oxygen,} & 8.\end{array}\right. \qquad \text{Litharge}\left\{\begin{array}{ll}\text{Lead,} & 102\cdot6.\\ \text{Oxygen,} & 8.\end{array}\right.$$

These three examples may serve to show that two elements may unite in different proportions to form two (or more) compounds; consequently an element may have *two or more*

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* The values are rounded off for the sake of clearness.

*equivalents.** It will be seen, however, that there is a simple relation between the two (or more) equivalents of any given element; in the examples just studied the higher one is a *simple multiple* of the other.

The results of the examination of many such cases in which two elements A and B unite in different proportions by weight are summarised in the **law of multiple proportions**: '*When any two elements A and B combine to form more than one compound, the weights of B which unite with any fixed weight of A stand to one another in the ratio of small whole numbers.*' This ratio is not necessarily 1:2 as in the above examples, but may be 1:3, 2:3, or any other simple ratio.

Since the proportions by weight in which elements combine are *always* equal to or simple multiples of their equivalents, it follows that 'when two elements A and B combine with one another, and also combine separately with any other element C, the weights of A, B, and C in *all* the compounds which they form are expressed by their equivalents or by simple multiples thereof.' This is known as *the law of reciprocal proportions.*

CHAPTER XX.

The Atomic Theory.

The law of multiple proportions was discovered by **John Dalton** (in 1804); the discovery led him to suggest a very important theory which would explain or account for this law, and also for the law of definite proportions (p. 53). Before considering this theory, the following rough mechanical illustrations of these two important laws may be considered.

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* If in the above examples the weight of oxygen combined with a *fixed* weight of the other element is calculated, then of course two equivalents of oxygen are obtained instead of two of the other element.

Imagine a large number of extremely small balls, all made of the stuff or matter of an element (A), say carbon, and all of the same weight; also a large number of balls of an element (B), say oxygen, all of the same weight. Let the *relative* weights of the A and B balls be 5·94 : 7·94, or in round numbers 6 : 8.

Now imagine that *one* of the A balls and *one* of the B balls attract one another and combine together, forming a paired or compound ball AB; and suppose, further, that some millions of these pairs are formed in a similar manner.

Then if any considerable weight of matter consisting of these compound balls AB were examined it would be found to have *constant properties;* if, in any way, the A balls could be separated from the B balls, the matter AB would be regarded as a compound; nevertheless it would be *constant* in *composition*, and would always consist of 6 parts by weight of A matter to 8 parts by weight of B matter, whatever sample was examined.

Imagine further that, under other conditions, instead of one A ball attracting only one B ball, it attracts and combines with *two*, and that some millions of these trios A,2B are formed; then if any considerable weight of matter composed of these compound balls A,2B were examined, it would be found to have *constant properties*; if, by any means, the A balls could be separated from the B balls, the matter would be regarded as a compound; nevertheless it would be *constant* in *composition*, and would always consist of 6 parts by weight of A to 16 parts by weight of B. If now the compositions of the pairs AB and the trios A,2B are considered, then, taking a *fixed* weight of B, say 8 parts, the weight of A in the pairs AB is 6, while in the trios A,2B it is 3; that is to say, if the balls A represent carbon matter, and the balls B oxygen matter, the compositions of the pairs AB and of the trios A,2B are those of carbon monoxide and carbon dioxide respectively (p. 177).

$$AB = \left\{ \begin{array}{l} A \ldots 6 \text{ parts by weight.} \\ B \ldots 8 \quad \text{"} \qquad \text{"} \end{array} \right.$$

$$A,2B = \left\{ \begin{array}{l} A \ldots\ 6 \\ 2B \ldots 16 \end{array} \right. \text{ or } \begin{array}{l} A \ldots 3 \text{ parts by weight.} \\ B \ldots 8 \quad \text{"} \qquad \text{"} \end{array}$$

These results would only be obtained so long as the balls did not get chipped or broken. If they were breakable (divisible), and pieces got broken off and separated, then any considerable weight of the matter AB or A,2B would *not* always consist of the same proportion of A and B matter; different samples would *differ* in properties, including composition, and the proportion of A combined with a fixed proportion of B matter would *vary indefinitely.*

If now, instead of carbon and oxygen matter, the balls A are composed of copper and B of oxygen matter respectively, and have the *relative* weights 31·5 : 8, then by making pairs AB a compound having the composition of black copper oxide, and by making trios 2A,B a compound having the composition of red copper oxide, would result (p. 178).

Similarly, with balls A of lead matter, and balls B of oxygen matter, having the relative weights 102·6 and 8, the pairs AB would have the composition of litharge, the trios A,2B the composition of lead dioxide (p. 178).

Now when two elements *combine*, the properties of the resulting compound are absolutely different from those of its constituents; in this respect the crude illustrations given above fail to give any idea of chemical combination, a fact which should be carefully borne in mind. This difficulty being ignored, and certain assumptions being made, the *compositions* of all the above combinations of different kinds of matter are in accordance with the laws of fixed composition and multiple proportions.

What assumptions have been made regarding these combinations?

1. That the stuff or matter of which an element consists is made up of small balls or *particles.*

2. That all the balls or particles of which an element con-

sists are of the *same weight*, but differ in weight from those of another element.

3. That the balls or particles cannot be broken or divided into smaller parts; that they are *indivisible.*

4. That the balls or particles combine with one another in *simple ratios.*

Such assumptions as these were made by Dalton, and to the indivisible, indestructible, extremely small particles, of which he supposed elements to consist, he gave the name '**atoms.**' These assumptions constitute the **Atomic theory**, of which the foundations were thus laid by Dalton.

According to this theory an *atom* is an *indivisible* part of an element; consequently it is the smallest mass of an element which can combine with any other element, or, in fact, take part in any chemical change. All the atoms of a given element have the same weight.

A *compound* is formed by the combination of atoms of different elements in some simple ratio; each particle of the compound so formed is called a **molecule**, and the molecule of a compound is thus the smallest weight of a compound which can exist.

It does *not* follow from the atomic theory that the atoms of an element are quite independent of one another; they may or may not form little groups or collections. In fact, there is evidence that in the case of many *free* elements their atoms do thus group themselves together; the smallest weight of an element which thus exists in the *free* (or uncombined) state is called a **molecule** of that element. Some elements may have molecules of single atoms only, others may form molecules each consisting of two atoms, and so on. These molecules, however, when they consist of more than one atom, may be resolved into their atoms when two elements combine, so that it is not the molecules but the atoms which unite together.

Chemical change may now be defined as a change which results in the formation of new molecules of an element or of a compound.

According to the atomic theory, when two elements A and B combine to form a compound, individual *atoms* of A combine with individual *atoms* of B; large, indefinite collections of atoms do not unite together. The simplest case is when *one* atom of one element unites with *one* atom of another. But an atom of one element may combine with two atoms of another, or with three, four, and so on; or two atoms of one element may combine with three of another, and so on.

Suppose, therefore, that two elements, say hydrogen and chlorine, which only form one compound, are caused to combine, and that one atom of hydrogen unites with one atom of chlorine to form a molecule of hydrogen chloride, then if there are more atoms, say, of hydrogen than of chlorine, the surplus or *excess* of hydrogen remains 'free,' and the result is a mixture of molecules of hydrogen chloride and of hydrogen. But the hydrogen chloride itself is always fixed in composition because it is formed of molecules all of which consist of one atom of hydrogen of definite weight and one atom of chlorine of definite weight.

Suppose, again, that two elements, say carbon and oxygen, which may form two compounds, are brought together under such conditions that one atom of carbon may combine either with *one* or with *two* atoms of oxygen; then *one* compound, or a mixture of *two* compounds, may be formed according to the relative proportions of the elements present. If the total number of carbon atoms is greater than that of the oxygen atoms some of the former remain as free carbon, whereas if the total number of oxygen atoms is more than double that of the carbon atoms some of the oxygen remains free. In any case the compound or compounds formed are fixed in composition, and the weights of carbon in the two compounds, combined with a fixed weight of oxygen, bear a simple ratio to one another, because the weights of the atoms and the numbers of each in the *molecule* are fixed. The atomic theory thus accounts for the laws of chemical combination.

Atomic Weights.

Since all the atoms of a given element have the same weight, but atoms of different elements have different weights, if an atom of each of the elements could be separately weighed, and the weight of each expressed in terms of some extremely small unit, the numbers thus obtained might be called the *atomic weights* of the elements. As, however, it is impossible to obtain a single atom, or to weigh one even if it could be obtained, the question arises: Is it possible to determine the *relative weights* of the atoms—that is to say, to ascertain how many times the atom of one element is heavier than that of another? This problem was considered by Dalton, and it will be useful to examine how he set about it.

Knowing that water is composed of 1 part by weight of hydrogen and 8 parts by weight of oxygen,* Dalton supposed that the molecule of water was composed of 1 *atom* of hydrogen and 1 *atom* of oxygen, in which case it is clear that the oxygen atom must be 8 times as heavy as the hydrogen atom, and the *relative* atomic weights are determined. In order to express these assumptions in a short way, Dalton used signs or *symbols* for the two elements, namely, the symbol ○ for oxygen and ⊙ for hydrogen, and represented the *molecule* of water by the combined symbols of the elements contained in it—thus, ○⊙. This collection of symbols, or **formula**, was intended to show that the molecule of water is made up of 1 atom of hydrogen and 1 atom of oxygen, and as each symbol represented also the *relative weight* of the atom of the element for which it stood, the formula also expressed the composition by weight of the compound water.

Again, knowing that carbon monoxide is composed of 6 parts of carbon to 8 parts of oxygen by weight, Dalton assumed that carbon monoxide was composed of 1 atom

* The most accurate value is 7·94 parts by weight of oxygen, while Dalton took it as 7; here and in several other cases whole numbers are given for the sake of simplicity, and Dalton's actual figures are not used.

of carbon and 1 atom of oxygen, and wrote its formula ● ○, the black circle representing 1 atom of carbon; carbon dioxide, which contains carbon and oxygen in the proportion 3 : 8 or 6 : 16, he represented by the formula ○ ● ○. If these assumptions are *facts*, then the *relative* weights of the atoms of hydrogen, carbon, and oxygen would be 1 : 6 : 8; and the three formulæ given above would express the compositions by weight of the three compounds water, carbon monoxide, and carbon dioxide respectively, because each symbol represents the relative weight of the respective atom. This idea of using a symbol for each of the elements was extended by Berzelius (in 1818), and is now generally employed. The symbol is usually the first letter of the name of the element; but when the names of two or more elements have the same initial letter, and the single letter has already been appropriated, then the first two letters form the symbol. Thus the symbol of carbon is **C**; of calcium, **Ca**; of copper (cuprum), **Cu**; and so on. A list of elements with their symbols is given later (p. 201). Compounds are then represented by writing side by side the symbols of the elements they contain, a small numeral after the symbol and below the line showing how many atoms of that element are present in the molecule; thus $\mathbf{CO}$ represents the molecule of carbon monoxide, $\mathbf{CO_2}$ that of carbon dioxide.

Returning now to the question of atomic weights, it has been noted that Dalton *supposed* or *assumed* that the molecule of water is composed of 1 atom of hydrogen and 1 atom of oxygen; its formula would then be $\mathbf{HO}$. But suppose that 2 atoms of hydrogen combine with 1 atom of oxygen; the formula of water would then be $\mathbf{H_2O}$, and as water is composed of hydrogen and oxygen in the proportion 1 : 8 by weight, the oxygen atom would be eight times heavier than 2 atoms of hydrogen, 16 times heavier than 1 atom of hydrogen; the relative atomic weights would not be 1 : 8 as supposed by Dalton, but 1 : 16.

Again, suppose that 3 atoms of hydrogen unite with 1 atom of oxygen; the formula of water would then be $\mathbf{H_3O}$, and the relative atomic weights 1 : 24. Lastly, suppose that 1 atom of hydrogen unites with 2 atoms of oxygen; then the formula would be $\mathbf{HO_2}$, and the relative atomic weights 1 : 4.

It must be evident, therefore, that the relative weights of the atoms of hydrogen and oxygen *cannot be determined* from an analysis of the compound which these elements form with one another unless it is known *how many* atoms of hydrogen and of oxygen have combined to form the molecule of water. The analysis of water merely gives the *equivalent* of oxygen—that is to say, the weight of oxygen which combines with 1 gram of hydrogen. If, however, the different *possible* values for the (relative) atomic weight of oxygen are considered, namely, 8, 16, 24, 4 (see above), it will be seen that they are all a simple multiple or a simple fraction of its equivalent ($E = 8$); and whatever be the (relative) atomic weight of oxygen, this relation *must hold:* (Relative) atomic weight $= n$E, where n is some simple whole number or some simple fraction.

The case of another hydrogen compound may next be considered. Hydrogen chloride is composed of hydrogen and chlorine in the proportion 1 : 35·2 by weight. Now if hydrogen and chlorine combine atom to atom, the formula of hydrogen chloride is $\mathbf{HCl}$, and the (relative) atomic weights of hydrogen and chlorine are 1 : 35·2. If, however, 1 atom of hydrogen combines with 2 atoms of chlorine, the formula is $\mathbf{HCl_2}$, and the (relative) atomic weights 1 : 17·6; if the formula is $\mathbf{H_2Cl}$, the (relative) atomic weights are 1 : 70·4; and so on. But in every case the (relative) atomic weight of chlorine is a simple fraction or a simple multiple of the equivalent ($E = 35{\cdot}2$); At. Wt. $= n$E.

Lastly, consider the case of the two oxides of carbon. In carbon monoxide the equivalent of carbon is 6. Then if the molecule of carbon monoxide is represented by the formula $\mathbf{CO}$, the (relative) atomic weight of carbon is 6 ($\mathbf{O} = 8$); if the formula is $\mathbf{C_2O}$, the (relative) atomic weight of carbon is 3; if $\mathbf{CO_2}$, then it is 12; and so on. In carbon dioxide the equivalent of carbon is 3. Then, if the formula is **CO**, the (relative) atomic weight of carbon is 3; if the formula is **CO_2**, the (relative) atomic weight is 6; if **CO_3**, then it is 9; and so on. The (relative) atomic weight of carbon, therefore, may be 3, 6, 9, 12, &c.—that is to say, a simple multiple or fraction of *both* (or all) its equivalents.

Hence the equivalents of an element, accurately determined by analyses of its compounds, are extremely important values, because the (relative) *atomic weight* of an element must be a simple multiple or simple fraction of all its equivalents: At. Wt. $= n$E.

Now the equivalents of all elements may be found experimentally, and, by various methods to be described later, the value of n in the above expression can be determined; the *relative* atomic weights, usually known as the **atomic weights** of the elements, are thus fixed in terms of some suitable standard, namely, the weight of an atom of hydrogen.

CHAPTER XXI.

The Law of Gay-Lussac.*

Since every compound has a fixed composition by *weight*, and since the *volume* occupied by a given weight of a given gas at N.T.P. is also fixed, it follows that when any compound is decomposed into gaseous elements, or when gaseous elements combine to form a compound, the relative volumes of these gaseous elements at N.T.P. are also constant.

Further, if a gaseous compound, A, is formed by the combination of a gaseous compound, B, with an element, C (as, for example, when carbon dioxide is formed from carbon monoxide and oxygen), the relative *volumes* of the product, A, and of the two gases, B and C, which unite, are also constant.

* Also known as Gay-Lussac's law of gaseous combination (or of combining volumes).

It follows, therefore, that whenever two (or more) gases are formed by the decomposition of a gaseous compound, or unite to form a gaseous compound, the volumes of all the gases concerned in the given change are always in the same fixed proportion.

About a century ago (1808) Gay-Lussac and Von Humboldt carried out a very important investigation in order to find experimentally the proportions by volume of the gaseous substances taking part in certain chemical changes. Some of the compounds they used have not yet been studied, so the results they obtained will be illustrated by other examples.

The compound hydrogen chloride is formed (with explosion) when hydrogen and chlorine are mixed together and an electric spark is passed through the mixture.

As chlorine cannot be collected over mercury (because it combines with this metal) and is soluble in water, this experiment has to be carried out under special conditions, and is a difficult one to perform.

It has been proved, however, that *one* volume of hydrogen combines with *one* volume of chlorine to form *two* volumes of hydrogen chloride, all the gases being measured under the same conditions of temperature and pressure.

When water (to which a few drops of sulphuric acid have been added) is decomposed with the aid of an electric current in a voltameter (p. 108) and the volumes of the liberated gases are measured under the same conditions, the volume of the hydrogen is always *double* that of the oxygen; it follows, therefore, that *two* volumes of hydrogen combine with *one* volume of oxygen to form the compound water.

This may also be proved as follows: Some pure dried hydrogen is passed up into a eudiometer (fig. 60, p. 162) filled with mercury, and its volume is carefully noted and corrected to N.T.P.; an approximately equal volume of pure dried oxygen is then passed into the same tube and the total volume of the mixed gases is noted and corrected to N.T.P.; by subtraction the volume of the oxygen is found.

The eudiometer is now pressed down on an india-rubber pad in the mercury-trough and firmly clamped in position, after which an electric spark is passed between the platinum wires (*a*, *a*); an explosion results, the gases combine, and most of the water which is formed condenses to a liquid—which then occupies a volume so relatively small that it may be neglected. On the eudiometer being slightly raised from the rubber pad, the mercury immediately rises in the tube and its level becomes constant; the volume at N.T.P. of the remaining gas is now ascertained (it is saturated with aqueous vapour, and the observed pressure must be corrected), and it can be proved that this gas is oxygen, free from hydrogen, as it is completely absorbed by phosphorus. Quantitative experiments of this kind show that *two* volumes of hydrogen always combine with *one* volume of oxygen; if either gas is present in excess of this proportion that gas remains unchanged.

If the combination of oxygen and hydrogen takes place at a temperature above the boiling-point of water and at atmospheric pressure, then the whole of the water remains in the state of vapour, and *its* volume may also be measured; it is then found that *two* volumes of hydrogen and *one* volume of oxygen combine to give *two* volumes of water vapour, all the gases being measured under the same conditions.

One limb of the eudiometer (*a*, fig. 67; compare also fig. 61, p. 162) is surrounded by a glass jacket (*b*), through which is passed from (*c*) the vapour of some liquid (amyl alcohol, for example) of boiling-point considerably higher than that of water; this vapour then passes through the condenser (*d*). Dry electrolytic gas (p. 109), which is known to be a mixture of two volumes of hydrogen and one volume of oxygen, is introduced into the eudiometer, and when the temperature is constant the mixture is brought to atmospheric pressure (compare p. 162). A spark is then passed through the gaseous mixture (observing necessary precautions), and after again adjusting the pressure the volume of the water vapour is noted; three volumes of the electrolytic gas give two volumes of water vapour.

The combination of carbon monoxide and oxygen to form carbon dioxide may also be examined volumetrically; it is then found that *one* volume of oxygen combines with *two* volumes of carbon monoxide to form *two* volumes of carbon dioxide.

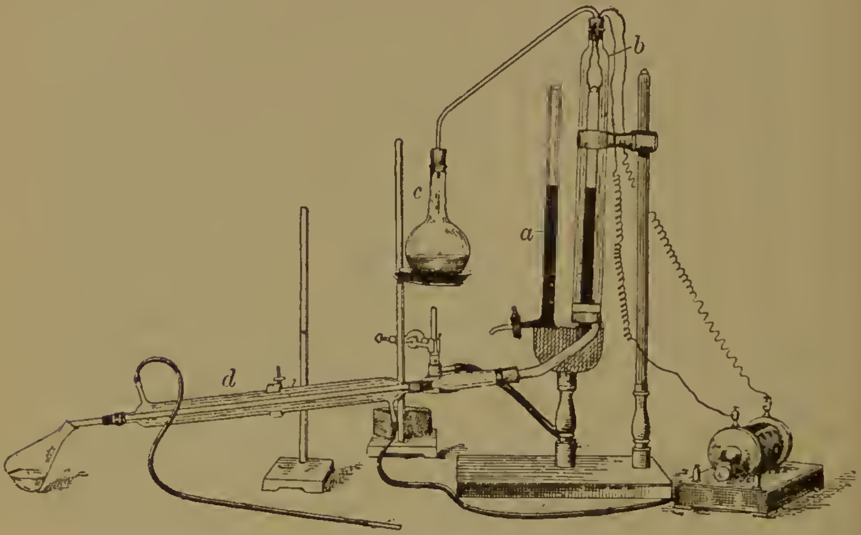

Fig. 67.

One of the gases is passed into the eudiometer (fig. 60, p. 162), and its volume (v_1) is noted and corrected to N.T.P. The other gas is then added, and the corrected volume (v_2) of the mixture is ascertained. The volume of the second gas is obtained by difference, and, for convenience, the *oxygen* ($v_2 - v_1$) is used in excess. The mixture is then exploded, and after the explosion the corrected volume (v_3) of the mixture of carbon dioxide and oxygen is ascertained; the diminution or *contraction* ($v_2 - v_3$) which has occurred is found by subtraction. A strong solution of sodium hydroxide is then passed up into the tube, whereupon the carbon dioxide is absorbed. The corrected volume (v_4) of the remaining gas (oxygen) is now ascertained, and the volume ($v_2 - v_1$) $-$ v_4 of this gas which has combined with the known volume (v_1) of carbon monoxide to form a known volume ($v_3 - v_4$) of carbon dioxide is thus determined.

Example:

Corrected volume of carbon monoxide (v_1), 20·4 c.c.
" " " " and oxygen (v_2), 40·1 c.c.
" " of oxygen ($v_2 - v_1$), 19·7 c.c.
" " after explosion (v_3), 29·9 c.c.
" " of oxygen (v_4) after absorbing carbon dioxide, 9·5 c.c.
" " of carbon dioxide formed ($v_3 - v_4$), 20·4 c.c.

Hence 19·7 – 9·5 = 10·2 c.c. of oxygen have combined with 20·4 c.c. of carbon monoxide to form 20·4 c.c. of carbon dioxide.

The results of many experiments of this nature led Gay-Lussac and Von Humboldt to the following important generalisation, which, tested and verified by numerous later investigators, is now known as **Gay-Lussac's law**: '*The relative volumes of the gaseous substances which take part in a chemical change are always expressed by some simple ratio.*'

It is possible to deduce this law without actually measuring the volumes of the gases, provided that their *densities* are known and also the composition by weight of the compound gas which is formed or decomposed in the given change. Thus, as it is known that the densities of hydrogen, chlorine, and hydrogen chloride are 1, 35·2, and 18·1 respectively, and that the composition of hydrogen chloride is H = 2·76, Cl = 97·24 per cent., the relative volumes of the hydrogen and chlorine which combine may be calculated. The volume of any gas required to give unit weight of that gas is inversely as its density; hence the volume of hydrogen required to give 2·76 g. of this element being $2{\cdot}76 \times \frac{v}{1}$, the volume of chlorine required to give 97·24 g. of chlorine is $97{\cdot}24 \times \frac{v}{35{\cdot}2}$; that is to say, the volumes must be *equal*. Further, since the density of hydrogen chloride is 18·1, which is the *mean* of those of its constituents, or $\frac{1+35{\cdot}2}{2}$, its volume must be *equal* to the *sum* of the volumes of the hydrogen and chlorine—that is to say, *two* volumes. Putting this in another way, since 2 volumes of hydrogen chloride weigh just the same as 1 volume of chlorine + 1 volume of hydrogen, no change in volume occurs when the elements combine.

Again, the densities of hydrogen and oxygen being known to be 1 : 15·88, and the composition of water being H = 11·2, O = 88·8 per cent., the *volumes* of the gases which combine must be in the ratio $11{\cdot}2 \times \frac{v}{1} : 88{\cdot}8 \times \frac{v}{15{\cdot}88}$, or as $11{\cdot}2 : 5{\cdot}6 = 2 : 1$. The density of water vapour is 8·94 (p. 161); since 2 volumes of hydrogen ($D = 1$) and 1 volume of oxygen ($D = 15{\cdot}88$) combine, there must be $\frac{1 + 1 + 15{\cdot}88}{8{\cdot}94} = 2$ volumes of water vapour.

In a similar manner the volume relationship may be calculated in other cases, and the results are expressed by the above law.

Now Gay-Lussac's law has a most important bearing on the atomic theory. According to this theory, when two elements unite to form a compound the individual *atoms* of the different elements combine in some simple ratio to form molecules of the compound; therefore the total *numbers* of the *atoms* of the elements which combine must also be in some *simple ratio.* But the *volumes* in which gaseous elements combine are also in some simple ratio; therefore the numbers of the atoms in equal volumes of different gaseous elements are in a simple ratio.

To make this reasoning clear, imagine two boxes of equal volume, one containing white, the other black balls (atoms), and that the balls are so small that their combined volume only fills a small fraction of the volume of the boxes; these balls may then represent the atoms or molecules of two gases (p. 182). Suppose now that one ball is taken from each box to make a compound ball ○●, and that this operation is repeated as long as possible; if then both boxes are emptied simultaneously, they must at first have contained equal numbers of balls (in the equal volumes).

Suppose next that the white balls (atoms) are originally joined in pairs (molecules), and that the black balls also form pairs, then if, on making the compound ○●, by separating the pairs and taking one white and one black ball, the boxes are emptied at the same time, the equal volumes must again have contained equal numbers of pairs (molecules).

Now imagine several boxes of equal volume, some containing white and some black balls, and that both kinds of balls are grouped in pairs (molecules), but that two black balls are taken to every single white one to form a compound ●○●; then, if exactly *two* boxes of black balls are emptied to every *one* box of white ones, the *three* boxes of equal volume contained equal numbers of pairs (molecules).

Lastly, suppose that the white balls form groups or molecules of three, while the black ones form molecules of two; then if, on breaking up these molecules and forming a compound ○●, exactly *three* boxes (volumes) of black balls are emptied to every *two* boxes of white ones, all the *five* boxes of equal volume contained equal numbers of molecules.

In all these cases the volumes in which the balls are contained are in a simple ratio, whether the balls are single or grouped in pairs or in sets of three.

These rough and unsatisfactory analogies may help to show that a most important conclusion may be drawn from the fact that gases combine together in simple proportions by volume.

CHAPTER XXII.

Avogadro's Hypothesis and the Law of Dulong and Petit.

It was pointed out by Avogadro (in 1811) that Gay-Lussac's law could be accounted for or explained by assuming that **equal volumes of all gases contain equal numbers of molecules,** under the same conditions of temperature and pressure; this most important generalisation is now known as **Avogadro's hypothesis** or theory, and is a necessary deduction from the kinetic theory of gases.

Unfortunately many years passed before the importance of this hypothesis was recognised, and it was not until it had been employed by Gerhardt and by Cannizzaro that its adoption became general.

With the aid of Avogadro's hypothesis the science of chemistry made great progress, for it now became possible to settle the relation between the equivalent and the atomic weight (p. 187) of an element.

In the first place, the *relative weights of the molecules* of elements and compounds could now be ascertained by direct weighing. If equal volumes of two different gases are weighed under the same conditions, since they contain equal numbers of molecules, *the relative weights of their molecules must be the same as the relative weights of the equal volumes.*

Now the *density* of a gas (compare footnote, p. 65) is the weight of the gas in terms of that of an equal volume of hydrogen; the density, therefore, also gives the relative weight of the *molecule* of the element or compound.

The densities of some gases are given in the following table. In the case of the gaseous elements, the equivalent of the element is also stated.

	Weight of 1 Litre at N.T.P. in Grams.	Density.	Equivalent.
Hydrogen	0·09	1	1
Oxygen	1·43	15·88	7·94
Chlorine	3·17	35·2	35·2
Nitrogen	1·25	13·9	4·63
Water (vapour)	0·80	8·9	—
Hydrogen chloride	1·63	18·1	—
Carbon dioxide	1·96	21·8	—
Carbon monoxide	1·25	13·9	—

A consideration of these values at once brings out an important fact, namely, that in the case of the elementary gases the density is a simple multiple of the equivalent; thus the density of chlorine is the same as its equivalent, that of oxygen is E × 2, that of nitrogen E × 3. The density, therefore, has some close connection with the *atomic weight* of an element, since the latter always bears a simple ratio to the equivalent (p. 187).

Now what is meant by atomic weight? It is a number expressing the weight of an atom of an element in terms of that of an atom of hydrogen; and an atom is the smallest weight of an element which can take part in the formation of a compound, or which can exist in the molecule of a compound.

If, then, the relative weights of the molecules of a number of compounds of hydrogen are determined by direct weighing, and the weight of hydrogen which is contained in these relative weights is known (from analyses), then those compounds which contain the *smallest* weight of hydrogen may be supposed to contain only one atom of that element in the molecule.

In the following table the actual and relative weights of one litre of different compounds of hydrogen, and of hydrogen itself, are given in columns I. and II. respectively; the actual weights of the hydrogen matter contained in a litre of the different gases (as determined by analysis) are given in column III. Several compounds which have not yet been described are included in the table in order to bring out more clearly the desired principle.

	I. Actual Weight of 1 Litre at N.T.P. in Grams.	II. Density (Relative Weight of Molecule).	III. Actual Weight of Hydrogen in 1 Litre.	IV. Relative Weight of Hydrogen in Litre, and therefore in Molecule.
Hydrogen chloride	1·63	18·1	0·045	1
Hydrogen bromide*	3·62	40·2	0·045	1
Hydrogen (free gas)	0·09	1·0	0·09	2
Hydrogen oxide (water vapour)	0·80	8·9	0·09	2
Hydrogen nitride† (or ammonia)	0·76	8·5	0·135	3
Hydrogen carbide‡ (or methane)	0·72	8·0	0·180	4

* A compound of hydrogen and bromine, very similar to hydrogen chloride.

† A compound of hydrogen and nitrogen (p. 260).

‡ A compound of hydrogen and carbon.

From this table it is seen that the weight of hydrogen in a litre of hydrogen chloride (and in a litre of hydrogen bromide) is less than the weight of hydrogen in a litre of any of the other compounds; that is to say, when the relative weights of the molecules of various hydrogen compounds are considered, and also the relative (or actual) weights of the hydrogen matter contained in these molecules, it is found that those of hydrogen chloride and of hydrogen bromide contain a smaller weight of hydrogen than any of the other molecules.

Now no known compound of hydrogen, in the state of gas or vapour, contains less than 0·045 g. of hydrogen in the litre; that is to say, no molecule is known in which there is a smaller weight of hydrogen than is present in the molecule of hydrogen chloride (and hydrogen bromide). As an atom is the smallest weight of an element which can exist in any molecule, it may be concluded that the molecule of hydrogen chloride (and that of hydrogen bromide) contains only *one atom* of hydrogen.

The atomic weight of hydrogen, therefore, might be arbitrarily fixed as 0·045. Such a value, however, would be highly inconvenient, and so the atomic weight of the standard element may be taken as a whole number and put = 1, 10, 100, or any other value; merely for the sake of simplicity the atomic weight of hydrogen is taken as 1.

Returning to the table (column IV.), it will be seen that the weight of hydrogen matter contained in a litre of *free* hydrogen or in the molecule of hydrogen is just double that of the hydrogen matter contained in a litre of hydrogen chloride or in the molecule of hydrogen chloride; hence the *molecule* of hydrogen consists of *two atoms.* The weight of a *molecule* of an element or compound in terms of that of one atom of hydrogen is called the **molecular weight** (M.W.); hence the molecular weight of hydrogen is 2.

Now, since 0·0899 gram of hydrogen occupies 1 litre, 2 grams (or one **gram-molecule**, or the molecular weight in grams) of hydrogen occupy 22·25 litres at N.T.P. (0·0899 : 2 : : 1 : $x = 22·25$).

But according to Avogadro's hypothesis the relative weights of equal volumes are also the relative weights of the molecules themselves; hence the number which expresses the weight in grams of 22·25 litres of any gas at N.T.P. also gives the molecular weight of that gas; **one gram-molecule of every gas occupies 22·25 litres at N.T.P.**

The data in the table (p. 195) may now be put more conveniently. The weight in grams of 22·25 litres of the gas is given in column III.; this number is the molecular weight of the gas, and it will be seen by comparing it with the density (column II.) that in all cases M.W. = D × 2.

	I. Weight of 1 Litre at N.T.P. in Grams.	II. Density.	III. Weight of 22·25 Litres in Grams. Molecular Weight.	IV. Weight of Hydrogen in the Gram-Molecule.
Hydrogen chloride	1·63	18·1	36·2	1
Hydrogen bromide	3·62	40·2	80·4	1
Hydrogen (gas)	0·09	1·0	2·0	2
Hydrogen oxide (water)	0·80	8·9	17·8	2
Hydrogen nitride (ammonia)	0·76	8·5	17·0	3
Hydrogen carbide (methane)	0·72	8·0	16·0	4

It is thus possible to find experimentally the molecular weight of any substance (element or compound) which can be obtained in the form of a gas or vapour; its density is determined (compare p. 159); and D × 2 = M.W.

The relation between density and molecular weight should be clearly understood. The density expresses how many times the molecule of the substance is heavier than a *molecule* (two atoms) of hydrogen; the molecular weight expresses how many times heavier the molecule is than one *atom* of hydrogen. The standard is two units in the first case, one unit in the other.

The determination of the atomic weights of other elements from the molecular weights of their compounds is based on the principle explained in the case of hydrogen. As large a number as possible of compounds of the element are analysed quantitatively; their densities are then determined, and from these their molecular weights. The smallest weight of the element in the *gram-molecule* of any of its compounds is then taken as its atomic weight, or rather the value thus determined shows what multiple of E must be taken in the expression At.Wt. = nE (p. 187). Thus in the case of oxygen data such as the following are obtained:

	Density.	Weight of 22·25 Litres at N.T.P. in Grams. Molecular Weight.	Weight of Oxygen in Gram-Molecule (by Analysis).	Relative Weight of Oxygen in Gram-Molecule.
Water (vapour) .	9	18	16	1
Carbon monoxide .	14	28	16	1
Oxygen (free gas) .	16	32	32	2
Carbon dioxide .	22	44	32	2
Sulphur dioxide (p. 229) . . .	32	64	32	2

These results, and similar ones obtained by studying many other compounds of oxygen, show that the smallest weight of oxygen in the gram-molecule of any oxygen compound is 16 (or more correctly 15·88); hence, as the *equivalent* of oxygen is 7·94, the atomic weight of the element is E × 2 = 15·88.

The *exact* value for the atomic weight of an element is *always* obtained from the equivalent. The determination of the density of a gas or vapour with great accuracy is a very troublesome and difficult task, and if the atomic weight were based directly on such determinations, its value might be very inaccurate owing to experimental error.* The equivalent, on the other hand, can be ascertained very accurately by the analysis of some suitable compound of the element, and then, knowing the approximate value of the atomic weight from the density determinations, the exact value is obtained by multiplying the equivalent by the factor indicated.†

The results contained in the above table also show that the *molecule* of oxygen consists of *two* atoms, so that its molecular weight is 32 (31·76). In a similar manner it is found that the molecules of *chlorine*, *nitrogen*, and of several other elements consist of *two* atoms. The molecules of some elements contain only one atom; those of others contain three, four, or more, as will be shown later.

Dulong and Petit's Law.

The method of determining atomic weights, based on the above principles, is only possible when the element forms a large number of gaseous or volatile compounds. Now by far the greater number of the elements are metals, and metals, as a rule, do not give many readily volatile compounds; their oxides, for example, cannot be converted into vapours, and of their simple derivatives only a few chlorides are volatile at high temperatures. Fortunately a very important method is known by which the atomic weights of such elements may be determined.

In times gone by, before the great importance of Avogadro's hypothesis was recognised, chemists gave arbitrary values to n in the expression At. Wt. $= n$E (compare p. 185), and thus obtained values for the atomic weights which might or might not be the true ones.

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* For the sake of simplicity many of the values for the absolute and relative weights of the gases given in the preceding tables are expressed in whole numbers.

† There is another reason why the atomic weight is not based directly on the density, namely, that the densities of gases are not *exactly* proportional to their molecular weights.

In 1818 Dulong and Petit discovered a most important connection between the specific heats* of the *solid* elements and their supposed or probable atomic weights, namely, that the specific heat × the probable atomic weight was approximately a constant, varying from *about* 6 to 7 (average value, 6·4);† in other words, the specific heat of a solid element is inversely proportional (approximately) to its atomic weight. Some data illustrating this discovery are given in the table:

	Specific Heat.	Atomic Weight.	Specific Heat × Atomic Weight.
Silver . . .	0·056	107·1	6·0
Iron . . .	0·11	55·5	6·1
Zinc . . .	0·094	64·9	6·1
Copper . .	0·092	63·1	5·8
Lead . . .	0·031	205·4	6·4

This fact could be accounted for by supposing that *all atoms have the same capacity for heat*, because the numbers of the atoms in equal weights of different elements are inversely proportional to the atomic weights of the elements.

This generalisation, **the law of Dulong and Petit,** may now be used to fix the approximate atomic weight of an element. The specific heat is determined experimentally, and the 'constant' 6·4 is divided by the value thus obtained. The result shows the *approximate* atomic weight only; but as At. Wt. = nE, the value of n is thus determined, and the *exact* atomic weight is then obtained from the equivalent.

For example, the equivalents of lead are 51·3 and 102·6; the specific heat of lead is 0·031. Now $\frac{6 \cdot 4}{0 \cdot 031} = 206 \cdot 4$, so that $n = 4$ or 2; hence the atomic weight of lead is 51·3 × 4 or 102·6 × 2, namely, 205·2.

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* The specific heat of a substance is the quantity of heat required to raise its temperature from 4° to 5° C., compared with that required to raise the temperature of an equal weight of water from 4° to 5° C.

† This product is called the *atomic heat.*

CHAPTER XXIII.

Empirical and Molecular Formulæ.

From their equivalents, by applying Avogadro's hypothesis and the law of Dulong and Petit, the atomic weights of nearly all the elements have been carefully determined; those of some of the better-known elements, together with their names and symbols, are given in the following table:

Name.	Symbol.	Atomic Weight.	Name.	Symbol.	Atomic Weight.
Aluminium	Al	26·9	Manganese	Mn	54·6
Argon	A	39·6	Mercury	Hg[4]	198·5
Barium	Ba	136·4	Nitrogen	N	13·9
Bromine	Br	79·4	Oxygen	O	15·9
Calcium	Ca	39·7	Phosphorus	P	30·8
Carbon	C	11·9	Potassium	K[5]	38·9
Chlorine	Cl	35·2	Silicon	Si	28·2
Copper	Cu[1]	63·1	Silver	Ag[6]	107·1
Hydrogen	H	1·0	Sodium	Na[7]	22·9
Iron	Fe[2]	55·5	Sulphur	S	31·8
Lead	Pb[3]	205·4	Tin	Sn[8]	118·1
Magnesium	Mg	24·2	Zinc	Zn	64·9

[1] Cuprum. [2] Ferrum. [3] Plumbum. [4] Hydrargyrum. [5] Kalium. [6] Argentum. [7] Natrium. [8] Stannum.

The composition by weight of a given compound being known, and also the atomic weights of the elements which are contained in it, is it possible to assign a formula (p. 184) to that compound?

Consider a simple case. The composition of hydrogen chloride is known, and also the atomic weights of hydrogen (1) and of chlorine (35·2). What is the formula of hydrogen chloride; that is to say, how many atoms of hydrogen and of chlorine are contained in the molecule of this compound? The composition of hydrogen chloride is $H = 2·76$, $Cl = 97·24$ per cent. As the chlorine atom is 35·2 times heavier than the hydrogen atom, if the percentage values are divided by the respective atomic weights the quotients express the *ratio* of the atoms in the compound, and therefore in the molecule,

$$\begin{aligned} \mathrm{H} &= 2{\cdot}76 \div 1 = 2{\cdot}76 \\ \mathrm{Cl} &= 97{\cdot}24 \div 35{\cdot}2 = 2{\cdot}76. \end{aligned}$$

As this ratio must be expressed by whole numbers (portions of atoms do not enter into chemical change), it is simplified (by dividing by the greatest common factor), and thus becomes 1 : 1. The simplest formula which would express the composition of hydrogen chloride, therefore, is HCl; such a formula, which merely shows the *ratio* of the atoms in the molecule, is termed an **empirical formula** (E.F.). But the *composition* of hydrogen chloride would also be expressed by the formula H_2Cl_2, H_3Cl_3, or $(HCl)_n$, where n is any whole number. How, then, is it possible to decide which of these formulæ represents the molecule of hydrogen chloride? By determining the *molecular weight* of hydrogen chloride.

Since the density of the gas is 18·1, its molecular weight is 36·2, and therefore the formula of its *molecule* must be HCl, because $1 + 35{\cdot}2 = 36{\cdot}2$. This formula, which expresses not only the ratio but also the actual numbers of the atoms of every element in the molecule, is called a **molecular formula** (M.F.), whether it is that of an element or of a compound.

When molecules of hydrogen chloride are formed, experiment shows that *one* volume of hydrogen combines with *one* volume of chlorine to give *two* volumes of hydrogen chloride. As it was on facts such as this that Avogadro's hypothesis was based, it may now be well to consider whether the conclusions drawn from this hypothesis are in agreement with the above fact. The conclusions are that the molecules of hydrogen, H_2 (and of chlorine, Cl_2, p. 199), contain two atoms of the element, and that the molecule of hydrogen chloride is HCl; the hypothesis is that equal volumes of these three gases contain equal numbers of molecules. Now suppose a litre of hydrogen contains x molecules (H_2); then a litre of chlorine contains x molecules (Cl_2), and a litre of hydrogren chloride also contains x molecules (HCl). But since every hydrogen molecule, also every chlorine molecule, contains *two* atoms, and every hydrogen chloride molecule only *one* atom, of each element, x molecules of hydrogen and x molecules of chlorine must give $2x$ molecules of hydrogen chloride. Further, since x molecules occupy one litre, $2x$ molecules occupy two litres; that is to say, the volume of the hydrogen chloride is double that of the hydrogen or that of the chlorine—a conclusion in accordance with the fact.

Consider next the case of water. Its composition is known to be $H = 11{\cdot}2$, $O = 88{\cdot}8$ per cent., and the atomic weights of hydrogen and oxygen are 1 and 15·88 respectively. What is the molecular formula of water? The empirical formula is first obtained by dividing the percentage values by the atomic weights of the respective elements, and then bringing the ratio to whole numbers,

11·2 [percentage of hydrogen] ÷ 1 = 11·2, and 11·2 ÷ 5·6 = 2
88·8 [percentage of oxygen] ÷ 15·9 = 5·6, and 5·6 ÷ 5·6 = 1.

The empirical formula is thus found to be H_2O, so that the molecular formula is $(H_2O)_n$, where n equals a whole number. But the density of water vapour is 8·94; therefore the molecular weight is 17·88, and the molecular formula must be $H_2O(1 + 1 + 15{\cdot}88)$.

When two volumes of hydrogen, H_2, and one volume of oxygen, O_2, unite, the result is two volumes of water, H_2O, in the state of vapour. As by Avogadro's hypothesis equal volumes of these three substances contain the same number (x) of molecules, if the molecular formula of water is H_2O, the volume of the water vapour must be the *same* as that of the hydrogen but *double* that of the oxygen, because for every molecule of water one *molecule* of hydrogen is required, whereas one *molecule* of oxygen suffices for the production of two molecules of water. In this case also the conclusions which have been based on Avogadro's law are in agreement with the facts.

These examples show how molecular formulæ are determined.* The composition of a compound and the atomic weights of the elements contained in it being known, the empirical formula is easily obtained. The molecular formula, however, remains unknown until the molecular weight of the substance has been determined from the density (or otherwise).†

As already stated (p. 198), the determination of the density is often attended by a considerable experimental error. This, however, is of very little importance, because the value for the molecular weight which is obtained from the density merely shows clearly what multiple of the empirical formula must be used in the expression $M.F. = (E.F.)_n$. The *exact* value for the *molecular weight* is then obtained by adding together the atomic weights of all the atoms in the molecule. Thus, if the density of water vapour were found to be 8·8 or 8·7, the molecular weight of water would not be taken as 17·6 or 17·4; this value merely shows that the value of n in the expression $M.F. = (H_2O)_n$ is 1. The exact molecular weight of water, therefore, is $1 + 1 + 15{\cdot}88 = 17{\cdot}88$.

EQUATIONS.

When the molecular formulæ of all the elements or compounds which take part in a given chemical change are known, and also the molecular formula of the product or products, the change may be represented both qualitatively and quantitatively in a very concise and complete manner.

If, for example, the combination of hydrogen and chlorine to form hydrogen chloride is expressed by,

$$H_2 + Cl_2 = 2HCl,$$

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* As an exercise, the molecular formulæ of carbon dioxide (p. 62) and of carbon monoxide (p. 120) respectively should be deduced from the data already given.

† Other methods for the determination of molecular weight will be described later.

where H stands for one atom of hydrogen and Cl for one atom of chlorine, the following facts are summarised: The molecule of hydrogen consists of two atoms; the molecule of chlorine consists of two atoms; two molecules of hydrogen chloride are formed from one molecule of hydrogen and one molecule of chlorine, and the molecule of this compound consists of one atom of each of the elements. Further, since the atomic weight of hydrogen is 1, and that of chlorine is 35·2, the expression shows that $1 + 1$ parts by weight of hydrogen combine with $35{\cdot}2 + 35{\cdot}2$ parts by weight of chlorine to form $2(1 + 35{\cdot}2)$ parts by weight of hydrogen chloride; the composition of hydrogen chloride by weight, therefore, is also given. Further, since equal volumes of all gases contain equal numbers of molecules, if one molecule of a gas, say hydrogen, occupies a certain volume, one molecule of every other gas occupies the same volume; hence the above expression also shows that one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrogen chloride. Further, since one gram-molecule of any gas occupies 22·25 litres at N.T.P., the above expression gives the *actual* as well as the relative volumes of the gases if the atomic weights are taken also as representing weights in grams. Since in every chemical change the sum of the weights of the original substances is *equal* to the sum of the weights of the products, the above expression is called an *equation.*

The equation representing the formation of water from its elements is written,

$$2H_2 + O_2 = 2H_2O,$$

and this equation shows that two molecules of hydrogen and one molecule of oxygen form two molecules of water; also that $2(1 + 1)$ parts by weight of hydrogen combine with $15{\cdot}88 \times 2$ parts by weight of oxygen to form $2(2 + 15{\cdot}88)$ parts by weight of water; also that two volumes of hydrogen combine with one volume of oxygen to form two volumes of water *vapour* (compare p. 189). The actual volumes of the different gases are also given if the atomic weights are taken as representing weights in grams; that is to say, 2 × 22·25 litres of hydrogen combine with 22·25 litres of oxygen to form 2 × 22·25 litres of water vapour.

Valency.—Before giving further examples of equations it may be pointed out that atoms of different elements do not always or even generally combine together in the simple ratio of 1 : 1; thus, although one atom of chlorine combines with *one* atom of hydrogen to form HCl, one atom of oxygen combines with *two* atoms of hydrogen to form H_2O, one atom of nitrogen combines with *three* atoms of hydrogen to form H_3N (ammonia), and one atom of carbon combines with *four* atoms of hydrogen to form H_4C (methane). Again, one atom of silver unites with *one* atom of chlorine to form AgCl (silver chloride), whereas one atom of calcium, zinc, or lead combines with *two* atoms of chlorine, forming the chloride $CaCl_2$, $ZnCl_2$, or $PbCl_2$, as the case may be; one atom of aluminium combines with *three* atoms of chlorine, and one atom of carbon with *four*.

Now if one atom of hydrogen or one atom of chlorine is taken as a measure of what may be called this atom-fixing capacity or *valency* of an element, then it is possible to class the elements as *uni- bi- ter-* or *quadri*-valent, according as the atom of that element combines with or fixes one, two, three, or four of the standard atoms. When this is done with some of the commoner elements the following list is obtained:

Univalent.	Bivalent.	Tervalent.	Quadrivalent.
Hydrogen, H Chlorine, Cl Sodium, Na Potassium, K Silver, Ag	Oxygen, O Sulphur, S Magnesium, Mg Calcium, Ca Zinc, Zn Lead, Pb Copper, Cu Mercury, Hg Manganese, Mn	Aluminium, Al Nitrogen, N Phosphorus, P	Carbon, C Silicon, Si Lead, Pb

According to this idea, when two univalent elements combine together they do so atom to atom, forming compounds such as HCl, $AgCl$, $NaCl$, KCl; one atom of a bivalent element combines with two atoms of a univalent element, forming compounds such as H_2O, H_2S, $CaCl_2$, Ag_2O, but with only one atom of another bivalent element, forming compounds such as CaO, MgO, PbS; one atom of a quadrivalent element combines with two atoms of a bivalent element, forming compounds such as CO_2; and so on.

This brief reference to the subject of valency is merely intended to assist the student in remembering particular formulæ and in writing equations. The valencies of the elements contained in a given compound or taking part in a chemical change being known, it is often possible to check such formulæ and equations and to avoid mistakes. If it is kept in mind, for example, that chlorine is univalent and calcium bivalent, the formula of calcium chloride could be correctly written $CaCl_2$, and incorrect formulæ such as $CaCl$, Ca_2Cl, $CaCl_3$ could be avoided. It must be pointed out, however, that the valency of an element is not constant. Thus copper is bivalent in cupric oxide, CuO, univalent in cuprous oxide, Cu_2O (compare pp. 177, 178); nitrogen and phosphorus may be either tervalent or quinquevalent (NH_3, PCl_3, NH_4Cl, PCl_5); lead is bivalent in some of its compounds (PbO, $PbCl_2$), quadrivalent in others (PbO_2); sulphur is bivalent (SH_2), quadrivalent (SO_2), or sexvalent (SO_3). It may also be noted that the valency of an element cannot, as a rule, be deduced by considering the molecular formula of a compound which consists of more than two elements; thus the formula of calcium carbonate, $CaCO_3$, and that of potassium chlorate, $KClO_3$, give no direct information as to the valency of any of the elements in the compounds.

The equations of some of the more important reactions already described may now be considered.

The combination of copper and oxygen to form cupric oxide, of lead and oxygen to form litharge, and of mercury and oxygen to form mercuric oxide, are expressed by the equations,

$$2Cu + O_2 = 2CuO, \qquad 2Pb + O_2 = 2PbO,$$
$$\text{and } 2Hg + O_2 = 2HgO$$

respectively, and these elements are all *bivalent* in these compounds.

The combination of litharge and oxygen to form red lead, and the reverse reaction, the decomposition of red lead (p. 81), are expressed by,

$$6PbO + O_2 \longleftrightarrow 2Pb_3O_4.$$

The decomposition of calcium carbonate into carbon dioxide and calcium oxide, and the combination of calcium oxide and water, are written respectively,

$$CaCO_3 = CO_2 + CaO \quad \text{and} \quad CaO + H_2O = Ca(OH)_2.$$

The use of brackets in the last case to express the fact that the molecule of calcium hydroxide contains two atoms of hydrogen and two atoms of oxygen is an alternative way of writing the formula CaO_2H_2 (compare p. 250).

The reaction which occurs in the formation of carbon dioxide from calcium carbonate and hydrochloric acid (p. 62) is written,

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O.$$

As it is known that calcium is bivalent and chlorine univalent, even if the equation could not be recalled to mind, it would be obvious that *two* molecules of hydrogen chloride are required to decompose *one* molecule of calcium carbonate.

The decomposition of potassium chlorate (p. 82) is expressed by,

$$2KClO_3 = 2KCl + 3O_2.$$

The molecule of potassium chlorate, as shown, is composed of one atom of potassium, one atom of chlorine, and three atoms of oxygen.

The formulæ of the oxides of phosphorus, magnesium, and iron (which are produced on burning the elements in oxygen, p. 84) are P_2O_5, MgO, and Fe_3O_4 respectively.

The formation of hydrogen from hydrogen chloride and zinc is expressed thus,

$$2HCl + Zn = H_2 + ZnCl_2;$$

and similar reactions occur with magnesium (Mg) and iron (Fe), both of which are bivalent in this change.

The formation of water from copper oxide and hydrogen ($CuO + H_2 = H_2O + Cu$), and the reversible reaction between water and iron ($4H_2O + 3Fe \longleftrightarrow Fe_3O_4 + 4H_2$), are important changes (pp. 105 and 106).

The double decompositions studied in the case of hydrogen chloride (p. 146) are expressed as follows,

$$2HCl + CuO = CuCl_2 + H_2O$$
$$2HCl + PbO = PbCl_2 + H_2O$$
$$2HCl + HgO = HgCl_2 + H_2O;$$

but in the formation of silver chloride from silver oxide and hydrogen chloride (p. 148) the equation is rather different, owing to the fact that silver is univalent,

$$2HCl + Ag_2O = 2AgCl + H_2O.$$

The action of hydrochloric acid on manganese dioxide (p. 140) is not a double decomposition, as three products are formed, namely, manganese chloride, chlorine, and water,

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

Many further examples of equations are given later.

As all equations are based on quantitative experiments, and express in a concise form, in terms of the atomic theory, the results of such experiments, it is absolutely unnecessary to commit to memory the relative weights or volumes of substances which take part in any change. These data are all given by the equation of the reaction, and can be calculated from it.

Thus, suppose it is required to know the weight of copper oxide which would be obtained from 100 g. of copper, and the equation of the reaction is known (p. 208), then, since $2Cu = 63{\cdot}1 \times 2$ and $2CuO = 2(63{\cdot}1 + 15{\cdot}88)$, it follows that 63·1 g. of copper give 78·98 g. of oxide, and consequently 100 g. of copper give $\frac{78{\cdot}98 \times 100}{63{\cdot}1} = 125{\cdot}2$ g. (compare p. 49).

Again, what weight of water would be obtained by burning 10 g. of hydrogen? Since $2H_2 = 2 \times 2$ and $2H_2O = 2(2 + 15{\cdot}88)$, it is known that 2 g. of hydrogen give 17·88 g. of water, and the required answer is 89·4 g.

Again, what *weight* of oxygen would be obtained, and how much potassium chloride would remain, if 150 g. of potassium chlorate are decomposed (p. 208)? Since $KClO_3 = 38{\cdot}9 + 35{\cdot}2 + (3 \times 15{\cdot}88)$, $2KClO_3 = 243{\cdot}5$ and $3O_2 = 95{\cdot}3$. Hence the weight of oxygen is $\frac{150 \times 95{\cdot}3}{243{\cdot}5}$.

$2KCl = 2(38{\cdot}9 + 35{\cdot}2)$, and the weight of potassium chloride, therefore, is $\frac{150 \times 74{\cdot}1 \times 2}{243{\cdot}5}$.

In calculating the *volume* of any gaseous substance from its *weight*, it is merely necessary to remember that the gram-molecule (the molecular weight in grams) occupies 22·25 litres at N.T.P. Thus, in order to find the *volume* of oxygen at N.T.P. obtained from 150 g. of potassium chlorate, $3O_2$ is now taken as $3 \times 22{\cdot}25$ litres; the required volume, therefore, is $\frac{150 \times 66{\cdot}75}{243{\cdot}5}$ litres.

In calculating the *weight* of any gas from its *volume*, it is only necessary to remember that the weight of a litre of any gas at N.T.P. is 0·09 g. × D; that is to say, the weight of a litre of hydrogen × the density of the gas, and $D = \frac{M.W.}{2}$. Thus the weight of a litre of chlorine, Cl_2, at N.T.P. is $0{\cdot}09 \text{ g.} \times \frac{70{\cdot}4}{2}$, and that of a litre of hydrogen chloride, HCl, $0{\cdot}09 \text{ g.} \times \frac{36{\cdot}2}{2}$.

The weight in grams of a litre of any gas at N.T.P. is also obtained by dividing the molecular weight of the gas by 22·25.

CHAPTER XXIV.

Sulphur and Hydrogen Sulphide.

In certain volcanic regions, notably in Sicily, a yellow crystalline 'mineral' is found in large beds or deposits, mixed more or less with limestone, gypsum, and other earthy matter. This yellow mineral is combustible, a most unusual property for a 'mineral,' and from very early times it attracted the attention of the alchemists, who called it *brenne-stone* or brimstone. The yellow crystals of brimstone consist of an *element* now known as **sulphur,** which melts, and then boils, when it is sufficiently heated. These properties are made use of in 'extracting' or separating sulphur from the earthy materials with which it occurs in nature.

For this purpose the sulphur 'ore' is made into heaps in shallow pits dug in the ground, and the sulphur is fired (ignited). The heat produced by slowly burning some of the sulphur in the material melts most of the remainder, which then collects at the bottom of the pit. This sulphur is impure, and is distilled from an iron retort. The vapour is condensed in brick chambers, where it collects as a fine yellow crystalline powder (sulphur snow), called *flowers of sulphur*, or as a liquid (when the chamber gets hot), which is afterwards run into cylindrical moulds (roll sulphur).

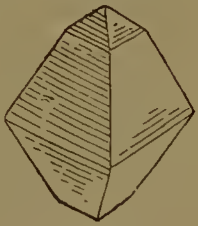
Fig. 68.

Sulphur is insoluble in water, but readily soluble in carbon disulphide, and when the filtered solution is evaporated slowly the element is deposited in transparent, amber-yellow *rhombic* (octahedral) crystals (fig. 68), which have a specific gravity of 2·07 and melt at 114·5°. The liquid obtained by heating pure sulphur just above its melting-point is of a pale, amber-yellow colour and quite mobile or fluid; but when it is gradually heated the colour darkens, and the yellowish-red liquid suddenly becomes so thick or viscous that it can hardly be poured. On being further heated, the liquid becomes a dark, brownish-red colour and more mobile, and finally begins to boil (at 448·4°), changing into a dark orange *vapour* which generally takes fire on coming into free contact with the air. When it cools, these changes in state, fluidity, and colour are reversed, until the pale, amber-yellow, mobile liquid is obtained again. This liquid, when further cooled, passes into a yellow or brownish-yellow crystalline solid, which might certainly be mistaken for ordinary (rhombic) sulphur. If, however, the *specific properties* of this yellow solid were examined it is possible that it would be found to have a melting-point of 120° (instead of 114·5°) and a specific gravity of 1·96 (instead of 2·07); that is to say, its specific properties would be different from those of 'ordinary' sulphur.

Now careful observations have shown that one of two *different* solid substances may be obtained by cooling pure melted sulphur. When the liquid is cooled very quickly, so that the solid is produced *below* 96°, octahedral crystals of ordinary sulphur are obtained; but when the liquid is kept *above* 96°, crystals of a different form (monoclinic), different melting-point (120°), and different specific gravity (1·96) are produced. This second form or variety of sulphur is generally prepared by melting sulphur in a deep basin and allowing the liquid to cool *slowly* until a crust has formed at the surface. This crust is then pierced, and the sulphur which is still liquid is poured off; on removing the crust long, brownish-yellow, transparent crystals of *monoclinic* sulphur are exposed. These crystals have been formed above 96°; they have the specific properties already given; but when kept at ordinary temperatures, even in a stoppered bottle, they gradually become opaque and break up into (aggregates of) very small octahedral crystals, identical in specific properties with those of ordinary sulphur. Conversely, when crystals of rhombic sulphur are kept above 96° (but below their melting-point) they gradually break up into aggregates of monoclinic crystals (m.p. 120°).

When commercial sulphur (which contains traces of impurities) is heated in a short-necked retort, and the boiling liquid sulphur which distils over is allowed to flow into water (fig. 69), so that it is *suddenly* cooled, it changes into a yellowish plastic or elastic substance of specific gravity 1·95, quite different from ordinary sulphur in outward properties. When kept for some days this *plastic sulphur* becomes hard and brittle; it has changed into masses of rhombic crystals (ordinary sulphur).

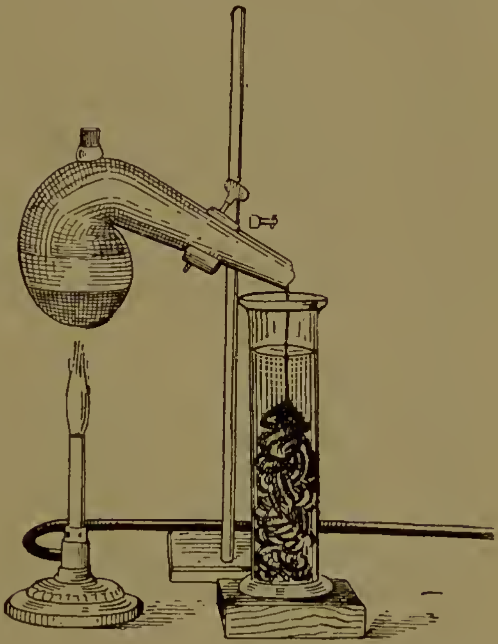

Fig. 69.

When plastic sulphur is treated with carbon disulphide only a part of it dissolves, leaving a pale-yellow insoluble powder, which must, of course, be different from ordinary sulphur. Hence plastic sulphur is a *mixture*, and the insoluble portion is called *amorphous* sulphur; from the solution rhombic sulphur is obtained. Flowers of sulphur contain a small proportion of amorphous sulphur. Amorphous sulphur is also present in the sulphur obtained from some of its compounds by precipitation. This form only changes into ordinary rhombic sulphur in the course of years, unless it is heated.

Dimorphism.—It can be proved experimentally that the different forms of sulphur described above consist of the *same matter;* when any one of these forms (rhombic, monoclinic, or plastic) is heated (out of contact with the air) it melts and gives liquid sulphur, from which ordinary rhombic sulphur is ultimately obtained. No change in weight, no gain or loss of matter, accompanies the conversion of one form into the other. The sulphur is not decomposed, and it does not combine with anything. Now the change solid sulphur $\longleftrightarrow$ liquid sulphur is merely a change in *state*, a physical change; the change of plastic or of monoclinic into rhombic sulphur, or the reverse change, may be similarly regarded.

Many substances, elements as well as compounds, resemble sulphur in forming two or more crystalline *modifications* or varieties, which differ more or less in all physical properties, as, for example, in melting-point and specific gravity, but which nevertheless are identical in *composition.* It may be supposed, therefore, that the difference between the various modifications is due to a difference in the *arrangement* of the particles of the substance in the crystal (compare footnote, p. 75). A substance such as sulphur or calcium carbonate which shows this behaviour is said to be *dimorphous* or *polymorphous* as the case may be. The different crystalline forms are produced at different temperatures and pressures, and as a rule each is permanent or *stable* only between certain limits of temperature and pressure; in that case one changes into the other when the conditions are so altered that it becomes *unstable.* Sometimes this change occurs very slowly, but it is generally hastened by rubbing, or by adding a crystal of the form which is going to be produced.

On comparing the behaviour of the element carbon with that of sulphur a close resemblance is brought to light; both exist in two crystalline varieties or modifications, and also in a third form which has not a definite crystalline structure.

The principal differences between the two cases are that whereas the various forms of sulphur pass into one another at temperatures easily reached, and only one of the forms is permanent (stable) at ordinary temperatures, graphite and diamond and charcoal are not changed except at extremely high temperatures.

When an *element* exists in two or more different forms which, like those of the element carbon, are more or less permanent under ordinary conditions, they are sometimes called *allotropic forms;* when, however, the different forms are easily changed into one another and are similar in chemical properties, they are usually termed *physical* forms or modifications.

Although the element sulphur, like the element carbon, thus occurs in forms which differ in specific properties, the property of changing in a fixed manner under fixed conditions is itself a very characteristic specific property of that variety of matter which is called sulphur.

Sulphur combines directly with many other elements. When merely placed in chlorine it is converted into chloride of sulphur; when heated in the air or in oxygen it takes fire and burns with a pale-blue flame, forming sulphur dioxide (p. 229). It also combines with most of the metals, forming compounds which are called **sulphides.** Thus when mercury and sulphur are well rubbed together **mercury sulphide** is formed. When a mixture of iron powder or filings and sulphur is heated gently, combination takes place rapidly with development of heat; the product, iron sulphide or **ferrous sulphide,** FeS, a black solid, is generally impure, even when equivalent quantities of the elements are used, and contains either free sulphur or free iron. When sulphur is heated to boiling in a tube, and a roll of copper gauze is plunged into its vapour, the gauze glows brightly and a black solid, **cuprous sulphide,** Cu_2S, is formed.

Sulphur is used in the manufacture of gunpowder, fireworks, matches, and vulcanite; also in the manufacture of sulphur compounds such as carbon disulphide.* Further, it is used to destroy fungi in vineyards, &c.

HYDROGEN SULPHIDE.

Sulphur and hydrogen do not combine at ordinary temperatures, but when sulphur is heated at about 310° in a closed tube filled with hydrogen the elements unite very slowly to form a disagreeably smelling gas, **hydrogen sulphide.** This gas occurs dissolved in some natural waters, such as those of Harrogate and elsewhere; it is also formed when animal matter, such as albumen, undergoes putrefaction, the smell of rotten eggs being partly due to the gas.

Hydrogen sulphide, mixed with hydrogen and other impurities, may be prepared from ferrous sulphide (p. 215) and diluted hydrochloric acid (or sulphuric acid). Small lumps of ferrous sulphide, covered with water and placed in a bottle or flask provided with thistle funnel and delivery-tube, as in fig. 21 (p. 66), are treated with a little concentrated hydrochloric acid.† Effervescence sets in, and the characteristic smell of hydrogen sulphide is soon recognised,

$$FeS + 2HCl = FeCl_2 + SH_2.$$

The gas is rather readily soluble in cold, but may be collected over *hot*, water; it is slightly heavier than air ($D = 17$), and may also be collected by displacing air upwards. It may be dried by passing it through tubes containing phosphorus pentoxide as it is decomposed by calcium chloride and by strong sulphuric acid.

Hydrogen sulphide is colourless; it burns in the air with a pale-blue flame, and a burning taper plunged into the gas is immediately extinguished. The inside of a glass cylinder in which the gas is burnt becomes covered with a pale-yellow film, which can be proved to be sulphur. A burning *jet* of the gas does not give a deposit of sulphur when a dry jar is held above the flame, but moisture condenses on the jar, and the strong smell of sulphur dioxide (p. 229) is recognised; hence hydrogen sulphide is a compound containing hydrogen and sulphur. When a cold object is moved slowly *through* a burning jet of the gas a film of sulphur is deposited on it. This behaviour is like that of some compounds of hydrogen and carbon (p. 133). At the temperature of its flame the hydrogen sulphide is decomposed, and in a plentiful supply of oxygen *both* the elements contained in it are finally converted into oxides, but when the air-supply is limited or the flame is cooled, the liberated sulphur is obtained in the free state. The flame is non-luminous because the sulphur is in the state of vapour (p. 133).

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* Carbon disulphide, CS_2, is manufactured by passing sulphur vapour over strongly heated carbon. It is a colourless liquid (b.p. 46°), and is highly inflammable.

† Compare footnote †, p. 62.

That hydrogen sulphide is very easily decomposed is proved by passing it through a glass tube which is heated gently with a Bunsen-flame; a deposit of sulphur is then obtained beyond the heated portion of the tube, and the escaping hydrogen may be ignited.

A convenient form of apparatus in which a confined volume of a gas may be *heated* is the eudiometer shown in fig. 60 (p. 162). With suitable electrical apparatus sparks may be passed between the ends of the two wires, and the gas is thus strongly heated just at this particular spot. Owing to diffusion and circulation, if the 'sparking' is continued long enough, the whole of the gas passes through this heated region, but owing to radiation and conduction the bulk of it remains practically at atmospheric temperature.

Now, when a given volume, say 20 c.c., of dry hydrogen sulphide is 'sparked' in this way for several hours, the gas is decomposed and a thin, pale-yellow deposit of sulphur is formed near the source of heat. The volume of the solid is so small in comparison with that of the hydrogen sulphide originally taken that it may be neglected, and yet the volume of the gas (hydrogen) in the tube is the same as that of the original compound, if measured under the same conditions.

This is another illustration of Gay-Lussac's law (compare p. 191). Since from any volume of hydrogen sulphide an equal volume of hydrogen is formed, and since equal volumes contain equal numbers of molecules, there must be *two* atoms of hydrogen in every molecule of hydrogen sulphide, because every molecule of hydrogen contains two atoms. Now the density of hydrogen sulphide is 17, and therefore its molecular weight is 34; as it is known that the atomic weight of sulphur is 32, the *molecular formula* of hydrogen sulphide is thus found to be SH_2,

$$\begin{gathered} SH_2 = H_2 + S \\ 1 \text{ vol.} = 1 \text{ vol.} \end{gathered}$$

It follows from Avogadro's hypothesis that if a gaseous element is liberated by decomposing any compound gas, or if, by combination, a gaseous element is converted into a gaseous compound, and the volume remains *unchanged*, the molecule of the element and that of the compound contain the same number of atoms of the gaseous element. Whether the whole of the hydrogen sulphide, or only a portion of it, is decomposed in the above experiment, the volume of the gaseous mixture remains constant, because every molecule of hydrogen sulphide gives one molecule of hydrogen.

The *solubility* of hydrogen sulphide in water at 15° is 323 (at 0°, 437), but the gas is completely expelled when its solution is boiled. The solution has the odour of the gas, and turns blue litmus red; it acts on certain metals, with liberation of hydrogen and formation of a *sulphide*.

The aqueous solution gradually becomes turbid, and gives a deposit of sulphur when it is kept, especially when exposed to air and sunlight; this decomposition is caused by atmospheric oxygen dissolved in the water,

$$2SH_2 + O_2 = 2S + 2H_2O.$$

Hydrogen sulphide is a very important 'reagent,' and is used in obtaining many sulphides.

A comparison of hydrogen sulphide with hydrogen chloride brings out certain similarities in properties. Thus, although hydrogen chloride is more active or vigorous than hydrogen sulphide, the aqueous solution of the latter has 'acid' properties, not unlike those of dilute hydrochloric acid. Hence hydrogen sulphide may also be called an *acid.* Now the hydrogen of hydrogen sulphide may be displaced by metals, by various methods described below. The compounds so formed, therefore, may be called 'salts,' just as are the substances produced from hydrogen chloride in a similar manner. These 'salts' of hydrogen sulphide are called *sulphides*, and although most of them may be obtained (in an impure form) by merely heating a metal with sulphur (just as chlorides may be obtained by heating a metal with chlorine), they may nevertheless be regarded as *derivatives* of hydrogen sulphide.

METALLIC SULPHIDES.

When silver is left exposed to the air of a town, it gradually becomes coated with a brown or black substance; this is *silver sulphide*, and its formation is due to the presence of traces of hydrogen sulphide in the atmosphere.

Silver sulphide may be prepared in various ways, as, for example, by heating silver with sulphur or in a stream of hydrogen sulphide; it is also obtained as a black *precipitate* when a stream of hydrogen sulphide is passed through a solution of silver nitrate. Its composition may be determined by taking a known weight of the metal, converting it into sulphide by one of these methods, and weighing the product; its percentage composition is thus found to be, silver 87·1, sulphur 12·9. The atomic weights of silver and of sulphur being known, the empirical formula is found to be Ag_2S,

87·1 [percentage of silver]
$\div 107{\cdot}1 = 0{\cdot}813$ and $0{\cdot}813 \div 0{\cdot}406 = 2$
12·9 [percentage of sulphur]
$\div\ 31{\cdot}8 = 0{\cdot}406$ and $0{\cdot}406 \div 0{\cdot}406 = 1.$

Many other metallic sulphides may be prepared by the three methods mentioned above; but the last one—namely, by passing hydrogen sulphide through a solution of a 'salt' of the metal—is generally used where possible, because the *precipitated* sulphide does not contain any free metal. When the solid metal itself is employed in preparing the sulphide, some of it may remain unchanged; for this reason a pure precipitated sulphide (antimony sulphide) is used instead of crude ferrous sulphide in preparing *pure* hydrogen sulphide.

Lead sulphide, PbS, is obtained as a black precipitate when hydrogen sulphide is passed through a solution of lead chloride,

$$PbCl_2 + SH_2 = PbS + 2HCl;$$

it is insoluble in water and in hydrochloric acid. *Mercuric sulphide*, HgS, and *cupric sulphide*, CuS,* are obtained as black precipitates on passing the gas through solutions of mercuric chloride, $HgCl_2$, and cupric chloride, $CuCl_2$, respectively; they are both insoluble in water and in hydrochloric acid.

When, on the other hand, hydrogen sulphide is passed through a solution of ferrous chloride, $FeCl_2$, no precipitate is formed, although ferrous sulphide is insoluble in water (compare p. 149). The reason of this is that ferrous sulphide is chemically soluble in dilute hydrochloric acid (p. 216); and as hydrogen chloride must be formed if ferrous chloride and hydrogen sulphide undergo double decomposition, it is impossible for ferrous sulphide to exist under the given conditions. For similar reasons sulphide of zinc cannot be obtained by such a method.

Many metallic sulphides occur in nature, sometimes in well-formed, pure crystals, but generally mixed with other sulphides and more or less earthy matter. Such 'minerals' have been known from early times, and have received distinct names; the metals are often extracted from them, and they are then called 'ores.'

Galena is an important ore of lead; it is found in black, lustrous crystals, and consists of **lead sulphide**, PbS, generally mixed with a very small proportion of silver sulphide.

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* This compound is not identical with cuprous sulphide, Cu_2S (p. 215).

Cinnabar is the principal ore of mercury, and consists of **mercuric sulphide**, HgS; it is dull red in colour, and is volatile, and can be *sublimed* (p. 19) out of contact with the air. When the sublimate is crushed it gives a fine scarlet powder, which is called *vermilion*, and is used as a paint, in colouring sealing-wax, &c. Although vermilion is so different in appearance from mercuric sulphide prepared by precipitation (p. 220), the scarlet and black substances are identical in *composition*.

Iron pyrites, FeS_2, occurs in golden-yellow crystals, and is often seen in lumps of coal; when left exposed to the atmosphere it is oxidised to ferrous sulphate (green vitriol, p. 226) and sulphuric acid. It is only very slowly acted on by hydrochloric acid, and in this respect particularly it differs from ferrous sulphide, FeS (p. 215). It is not an iron 'ore,' but is used in the manufacture of sulphuric acid (p. 287).

Zinc blende is a shining, yellow, brown, or black mineral which consists principally of **zinc sulphide**, ZnS, and is one of the important ores of zinc. Its brown or black appearance is due to the presence of sulphides of iron and other metals.

The behaviour of metallic sulphides when they are heated in the air (roasted) is referred to later (p. 229).

CHAPTER XXV.

Hydrogen Sulphate, Sulphuric Acid, or Oil of Vitriol, and its Salts.

The substance known as **sulphuric acid**, which was first obtained by strongly heating green vitriol (p. 39), is now manufactured in very large quantities by two other processes (pp. 232, 287), and is a most important compound.

The commercial acid, still called 'oil of vitriol,' is a rather thick, oily liquid of sp. gr. *about* 1·8. When left exposed to the air it absorbs aqueous vapour from the atmosphere, as it is very hygroscopic (p. 38); hence its use in drying various gases. When heated in an open vessel on a water-bath it does not volatilise; but at higher temperatures it distils, passing over between, say, 280° and 330°. As the commercial acid has not a constant boiling-point, it may be inferred that it is a mixture or that it decomposes. If a 'fraction' of the acid which distils at about 330° is collected separately and cooled sufficiently it deposits crystals; and if these are melted and frozen again several times, the mother-liquor being separated after each operation, pure **sulphuric acid** or **hydrogen sulphate** is obtained as a colourless solid, melting at 10° to a liquid of sp. gr. 1·84 at 15°. The pure acid fumes when it is heated, and begins to boil at about 290°, the boiling-point gradually rising to 330°; this behaviour shows that hydrogen sulphate is *decomposed* when it is heated.

Ordinary liquid sulphuric acid is a solution of the compound hydrogen sulphate in a little water, but the commercial acid also contains small quantities of *lead sulphate* and other impurities. Sulphuric acid, unless very much diluted with water, causes severe burns when placed on the skin, and it attacks and decomposes most animal and vegetable compounds, turning them black and liberating carbon; for example, when concentrated sulphuric acid is poured into a warm, saturated solution of cane-sugar, rapid charring occurs, the sugar being completely decomposed, principally into carbon and water.

Sulphuric acid is miscible with water, the operation being accompanied by a great development of heat.* The volume of the 'dilute' acid is less than the combined volumes of its components; that is to say, a contraction has taken place. These facts seem to show that sulphuric acid *combines* with water and does not merely dissolve.

Dilute sulphuric acid has a sour taste, and changes the colour of blue litmus to red. Pure sulphuric acid, and even the commercial acid, which may contain as much as 20 per cent. of water, has very little action on common metals such as zinc, iron, copper, mercury, and silver at ordinary temperatures; but when heated with such metals a rapid action sets in, and a gas, *sulphur dioxide*, is evolved (p. 229). When, however, the acid is mixed or diluted with several times its own volume of water, it acts on zinc, iron, and magnesium (but not on copper, mercury, or silver) at *ordinary temperatures*, giving *hydrogen* and a *sulphate* (see below) of the metal. It seems very extraordinary that mixing the acid with water should enable it to attack some metals at ordinary temperatures, but it can be proved that the liberated hydrogen really comes from the acid and not from the water (compare p. 225). The action of *concentrated* sulphuric acid on metals is described later (p. 230).

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* For this reason, in diluting the acid, the acid is always added slowly to the water, and not *vice versâ*, as this might cause boiling and spirting.

SULPHATES.

When zinc, iron, or magnesium is placed in a given quantity of dilute sulphuric acid, the metal is rapidly attacked at first and hydrogen is evolved; but if more of the metal is added from time to time, the action gradually slackens and at last ceases altogether. As the metal now remains in the liquid without being attacked, it may be concluded that the solution no longer contains sulphuric acid. On filtering and concentrating such a solution, crystals are obtained. When the *oxide* of a metal is placed in a given quantity of dilute sulphuric acid it dissolves chemically, but no evolution of hydrogen occurs. On more oxide being added from time to time the action finally ceases, because all the sulphuric acid has been changed. On filtering and concentrating such a solution, crystals are obtained.

The crystals thus formed from a given metal and sulphuric acid are identical with those formed from the oxide of the metal, provided that in the case of a metal which forms more than one oxide one particular oxide is taken.

Now, since the metal liberates hydrogen as gas, but the oxide does not, if the corresponding results obtained with hydrochloric acid (p. 146) are considered it may be presumed (*a*) that sulphuric acid contains combined hydrogen, which may be displaced by a metal, and (*b*) that when sulphuric acid acts on an oxide the combined hydrogen of the acid and the combined oxygen of the metallic oxide unite to form water—in fact, that double decomposition occurs (p. 147).

The compounds thus formed by displacing the combined hydrogen of the acid, hydrogen sulphate, by metals belong to the class of compounds called 'salts,' and are grouped together as the *sulphates.*

Silver sulphate.—When silver oxide is dissolved chemically in hot, dilute sulphuric acid and the concentrated solution is cooled, colourless crystals of silver sulphate are obtained. The same compound is formed when silver sulphide (p. 219) is gently heated in a stream of pure oxygen; hence silver sulphate is a compound of silver, sulphur, and oxygen.

The composition of silver sulphide being known, that of silver sulphate may be determined by converting a known weight of the sulphide into sulphate. For example, 10 g. of silver sulphide (known to contain 8·71 g. of silver and 1·29 g. of sulphur, p. 219) give 12·58 g. of silver sulphate; hence 12·58 g. of silver sulphate are composed of 8·71 g. of silver, 1·29 g. of sulphur, and 2·58 g. of oxygen. These values being divided by the atomic weights of the respective elements, the empirical formula of silver sulphate is found to be Ag_2SO_4,

$$\begin{array}{ll} 8{\cdot}71 \text{ [percentage of silver]} & \div 107{\cdot}1 = 0{\cdot}0813 \\ 1{\cdot}29 \text{ [percentage of sulphur]} & \div \ \ 31{\cdot}8 = 0{\cdot}0406 \\ 2{\cdot}58 \text{ [percentage of oxygen]} & \div \ \ 15{\cdot}9 = 0{\cdot}1624 \end{array}$$

$$\text{and } 0{\cdot}0813 : 0{\cdot}0406 : 0{\cdot}1624 \text{ as } 2 : 1 : 4.$$

Now, since silver sulphate is formed, together with water, from silver oxide and sulphuric acid (by double decomposition), and since it is known that one atom of univalent silver displaces one atom of hydrogen (silver chloride has the formula

AgCl), the empirical formula of sulphuric acid (hydrogen sulphate) is thus found to be H_2SO_4,

$$H_2SO_4 + Ag_2O = Ag_2SO_4 + H_2O.$$

It can be proved by further experiments (but *not* by vapour-density determinations, because sulphuric acid decomposes when it is strongly heated, p. 222) that this is also the molecular formula of sulphuric acid.

This is an example of indirect analysis. Hydrogen sulphate itself is not easily handled, as it is so hygroscopic. It cannot be accurately analysed by any simple, direct method; therefore its percentage composition and empirical formula are determined by analysing one of its *derivatives*, the relation of which to hydrogen sulphate itself is known. The action of dilute sulphuric acid on certain metals and their oxides is therefore expressed by equations such as the following,

$$Zn + H_2SO_4 = ZnSO_4 + H_2; \quad Mg + H_2SO_4 = MgSO_4 + H_2$$
$$ZnO + H_2SO_4 = ZnSO_4 + H_2O; \quad MgO + H_2SO_4 = MgSO_4 + H_2O$$
$$Ag_2O + H_2SO_4 = Ag_2SO_4 + H_2O;$$

and it will be seen that one atom of the bivalent metals, zinc and magnesium, displaces two atoms of hydrogen, whereas the univalent silver atom only displaces one.

Copper sulphate has already been mentioned several times (pp. 36, 46); it is a very important sulphate, and is used in large quantities in agriculture for killing moulds which grow on the vine and other plants. Although copper is *not* acted on by hot dilute sulphuric acid, it gradually dissolves chemically if air (oxygen) is blown through the liquid, and this fact is made use of in preparing blue vitriol on the large scale.

The blue crystals (blue vitriol) obtained by evaporating the solution contain 36·07 per cent. of water of crystallisation and 63·93 per cent. of cupric sulphate (p. 37); dividing these percentages by the *molecular* weights of water and cupric sulphate respectively, the results show that the crystals contain five molecules of water to every molecule of copper sulphate,

$$36{\cdot}07 \text{ [percentage of } H_2O] \div 18 = 2{\cdot}004$$
$$63{\cdot}93 \text{ [percentage of } CuSO_4] \div 159{\cdot}5 = 0{\cdot}4008$$
$$\text{and } 2{\cdot}004 : 0{\cdot}4008 \text{ as } 5 : 1.$$

The composition of the blue crystals, therefore, is expressed by the formula $CuSO_4$, $5H_2O$.

In the case of every substance which contains water of hydration, not only is the proportion of the latter *constant* when the crystals have been formed under fixed conditions, but it is also such that the relative numbers of the molecules of the two compounds (water and anhydrous substance) may be expressed by some fairly simple ratio. Thus the composition of *hydrated* crystals of calcium chloride is $CaCl_2$, $6H_2O$, and the highly hygroscopic character of *anhydrous* calcium chloride may be ascribed to its power of thus fixing water.

Ferrous sulphate, $FeSO_4$, $7H_2O$ (green vitriol, p. 221), is prepared by dissolving scrap-iron in dilute sulphuric acid and then concentrating the solution until the salt crystallises out. The crystals are efflorescent (p. 38), and are used in dyeing, and in making black inks.

Zinc sulphate, $ZnSO_4$, $7H_2O$ (white vitriol), is colourless and readily soluble in water.

Magnesium sulphate, $MgSO_4$, $7H_2O$, is contained in many spring- and river-waters (p. 281), and is known as Epsom salt from its occurrence in large quantities in a mineral spring at Epsom. It forms large, colourless crystals, and is very readily soluble in water.

Sodium sulphate, Na_2SO_4, $10H_2O$, known also as 'Glauber's salt,' is also very readily soluble, and occurs in spring- and river-waters.

Calcium sulphate, $CaSO_4$, occurs as a rock or mineral called *anhydrite*, which consists principally of anhydrous calcium sulphate, and also as the mineral *gypsum* or *selenite*, which consists of hydrated calcium sulphate, $CaSO_4 + 2H_2O$, and sometimes occurs in well-formed, colourless, transparent crystals. Gypsum is very abundant. When it is heated at about 125° some of the water of hydration is expelled, and the white residue, when powdered, is known as Plaster of Paris. This powder takes up water of hydration again when it is mixed with water, and in doing so sets to a moderately hard mass. Plaster of Paris, therefore, is used in making casts of different objects; also as a cement for ornamental work.

Calcium sulphate is only sparingly soluble (1 in 500 at 18°) in water, but it is contained in many spring- and river-waters (in which it causes 'permanent hardness,' p. 281).

Barium sulphate, $BaSO_4$, which occurs as a white crystalline mineral called *heavy-spar*, is insoluble in water and also in hydrochloric or nitric acid; these facts are made use of in distinguishing barium sulphate from other white earthy materials, such as chalk, calcium sulphate, &c. When aqueous solutions of barium chloride and sulphuric acid are mixed, barium sulphate is precipitated,

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl,$$

and although the solution then contains hydrochloric acid, this acid does not affect the precipitate. Barium sulphate is also precipitated when a solution of *any sulphate* is added to a solution of barium chloride,

$$BaCl_2 + Na_2SO_4 = BaSO_4 + 2NaCl.$$

As barium sulphate is insoluble, a precipitate is formed even when a very dilute solution of sulphuric acid or a sulphate is treated with a solution of barium chloride; hence it is possible to test for sulphuric acid or a sulphate by adding barium chloride (and then hydrochloric acid), and in this way the presence of sulphates is shown in nearly all natural waters except rain-water.* Further, since barium sulphate is insoluble in water and in hydrochloric acid, it follows that when excess of barium chloride is added to a solution of a sulphate, the *whole* of the latter undergoes double decomposition (p. 149) and is precipitated in the form of barium sulphate; hence the *weight* of sulphuric acid (hydrogen sulphate) or of any sulphate contained in a given solution may be *estimated* by first adding dilute hydrochloric acid (to prevent any other salt from being precipitated) and then excess of barium chloride, filtering, washing, and weighing the dried precipitate.

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* If necessary the extremely dilute solution (natural water) may be first concentrated by evaporation.

As it is known that the formation of barium sulphate * from sulphuric acid and barium chloride is expressed by the equation just given, and that the molecular weights of sulphuric acid and barium sulphate are 98 (1 + 1 + 32 + 64) and 232·4 (136·4 + 32 + 64) respectively, it is obvious that 232·4 g. of precipitate are obtained for every 98 g. of sulphuric acid present. Similarly 232·4 g. of barium sulphate are obtained for every 142 g. of sodium sulphate,† and so on.

Radicles.—Hydrogen sulphate and all the metallic sulphates described above contain one atom of sulphur and four atoms of oxygen, and as one sulphate can often be changed into another by double decomposition, it would seem that the atom of sulphur and four atoms of oxygen hang together, as it were, forming the foundation (or root) of a number of compounds. The term *radicle* is applied to any collection or *group of atoms* which thus occurs in a number of different compounds, and which may be transferred from one to another. When such a group, combined with hydrogen, forms an acid, it is called an *acid radicle*, and, as the radicle SO_4 is always combined with two atoms of hydrogen, or the equivalent of two atoms of hydrogen (Ag_2, Ca, Zn, Fe, &c.), it is a *bivalent* radicle.

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* The composition of barium chloride (p. 148) may be determined by treating a weighed quantity with excess of silver nitrate and weighing the silver chloride so formed (p. 149). The percentage of barium in the sulphate may then be determined by treating a weighed quantity of barium chloride with excess of sulphuric acid and weighing the barium sulphate. Both reactions are carried out in aqueous solution.

† The percentage of sodium sulphate would be expressed in terms of the *anhydrous* salt Na_2SO_4, *not* $Na_2SO_4, 10H_2O$ (p. 226).

CHAPTER XXVI.

Sulphur Dioxide and Sulphur Trioxide.

Sulphur burns in the air (or in pure oxygen) with a blue flame, combining with the oxygen to form an invisible gas, **sulphur dioxide**, which is easily recognised by its characteristic, suffocating smell. This gas is also formed, together with water, when hydrogen sulphide burns in a free supply of air; also when many metallic sulphides are heated in the air, or *roasted*, the metal being changed into an oxide,*

$$S + O_2 = SO_2; \quad 2SH_2 + 3O_2 = 2SO_2 + 2H_2O;$$
$$2ZnS + 3O_2 = 2ZnO + 2SO_2.$$

The gas obtained by any of these methods is, of course, mixed with nitrogen, and generally with oxygen as well. The pure gas is prepared by heating copper, mercury, zinc, or sulphur with concentrated sulphuric acid in an apparatus such as that shown in fig. 54 (p. 140); it is collected over mercury, as it is readily soluble in water, or by displacing air upwards. Sulphur dioxide is not inflammable, and ordinary burning substances are extinguished by it. It is very easily liquefied by pressure, and in this state is sold in glass bottles (fig. 70). When the tap of such a bottle is opened the *gas* escapes, and as the pressure is reduced the liquid changes into the gas.

Sulphur dioxide, like carbon dioxide, is completely absorbed by soda-lime. When a weighed quantity of *pure* sulphur is completely burnt in a stream of oxygen, and the product (or products) is absorbed in a weighed soda-lime tube, it is found that 1 g. of sulphur gives rather more than 2 g. of product, but the results are not *quite* constant.

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* Most sulphides behave in this way, but some combine directly with oxygen and are partly or entirely changed into sulphates, $CaS + 2O_2 = CaSO_4$.

The atomic weights of sulphur and of oxygen being known, it may be *calculated* that an oxide of the formula SO would contain 66·6 per cent. of sulphur and 33·3 per cent. of oxygen, an oxide of the formula SO_2, 50 per cent. of each element. It seems clear, therefore, that under the above conditions (since 1 g. of sulphur gives rather more than 2 g. of sulphur dioxide) the principal product is an oxide, SO_2. Now the density of pure sulphur dioxide (obtained from copper and sulphuric acid) is 32, so that the molecular weight is 64, corresponding with the molecular formula SO_2. How is it, then, that 1 g. of sulphur does not always give *exactly* 2 g. of sulphur dioxide? Careful investigations have shown that small and variable quantities of another oxide of sulphur (SO_3) are produced under the above conditions. When the formation of this second product is allowed for, it is found that 2 g. of sulphur dioxide are in fact produced from—or contain—1 g. of sulphur.

When copper is heated with strong sulphuric acid the metal disappears, but instead of hydrogen (as might be expected) only sulphur dioxide, SO_2, is evolved. If the dark liquid which remains after this action is poured into a little water, filtered, and evaporated, blue hydrated crystals of copper sulphate are obtained. How is it that some metals dissolve chemically in *dilute* sulphuric acid, liberating hydrogen and giving a metallic sulphate, whereas the same metals and others when heated with *strong* sulphuric acid give sulphur dioxide and a sulphate? What becomes of the combined hydrogen of the acid in the latter case?

It may be supposed that at high temperatures two distinct changes take place: (*a*) the acid is decomposed by the copper with formation of copper oxide, water, and sulphur dioxide; (*b*) the copper oxide and more sulphuric acid give copper sulphate and water,

$$(a)\ Cu + H_2SO_4 = CuO + H_2O + SO_2$$
$$(b)\ CuO + H_2SO_4 = CuSO_4 + H_2O.$$

These being combined in one equation, the final result is,

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

Similar changes occur in the case of mercury, zinc, silver, and some other metals. That the sulphuric acid is probably decomposed in this way is shown by the fact that the elements sulphur and carbon, which do *not* displace hydrogen from any acid, and which are not acted on by acids as a class, may be used instead of a metal in preparing sulphur dioxide,

$$(a)\ S + 2H_2SO_4 = 2SO_2 + 2H_2O + SO_2\ (\text{or } 3SO_2 + 2H_2O)$$
$$(a)\ C + 2H_2SO_4 = 2SO_2 + 2H_2O + CO_2.$$

The change (*b*) does not occur in these cases.

There are many chemical operations in which a given product is obtained owing to the occurrence of two or more distinct changes or reactions, which may be supposed to follow one another in a fixed order; the changes are then termed primary, secondary, &c. Thus the formation of sulphur dioxide, water, and copper oxide may be regarded as the primary change or reaction in preparing sulphur dioxide, and the formation of copper sulphate as a secondary change.

SULPHUR TRIOXIDE.

When sulphur dioxide is mixed with oxygen in variable proportions no sign of chemical change is observed, the mixture does not take fire when a light is applied to it, and if passed through a red-hot tube the mixture still smells strongly of sulphur dioxide, all of which facts show that the two gases do not combine together very readily or rapidly. Careful observations, however, prove that a small quantity of a new substance is formed when the gases are heated together.

A very different result is obtained when a mixture of the gases, carefully dried with sulphuric acid, is led through a glass tube (fig. 70) containing some asbestos (at *d*), which has been covered with very small particles of *platinum*, and which is heated with a Bunsen-flame; a beautiful, colourless, crystalline solid collects in the receiver (*e*), and if the volume of oxygen in the mixture is about half that of the sulphur dioxide, very little *gas* escapes from the bottle (*f*);* that is to say, most of the gaseous mixture is changed into a solid substance. The compound formed in this way is **sulphur trioxide.** When it is dropped into water a hissing sound (caused by the sudden formation of steam) is heard, and it gives a colourless solution with great heat development. If the addition of sulphur trioxide is continued, a thick, oily liquid identical with sulphuric acid is formed.

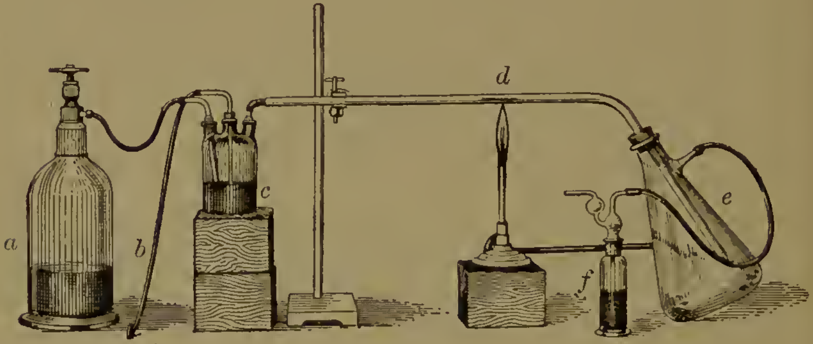

Fig. 70.

These are the principles of one method—the *contact process*—for the manufacture of sulphuric acid. A mixture of sulphur dioxide and air, carefully purified, is passed over heated platinised asbestos, and the product is dissolved in water.

The formation of sulphur trioxide from sulphur dioxide and oxygen proves that the trioxide contains a larger proportion of oxygen than the dioxide. As the trioxide combines with water to form sulphuric acid, and no gas is evolved in the process, sulphur trioxide must have the formula, SO_3 $[2SO_2 + O_2 = 2SO_3]$,

$$SO_3 + H_2O = H_2SO_4.$$

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* The siphon or bottle (*a*) contains liquid sulphur dioxide under pressure; the tube (*b*) is connected with a cylinder of oxygen. Both gases are dried by bubbling them through sulphuric acid contained in (*c*), where they are also mixed. The bottle (*f*) contains sulphuric acid to prevent the entrance of moisture.

An oxide, such as sulphur trioxide, which combines with water to form an acid is called an **anhydride.** Sulphur trioxide is *sulphuric anhydride.* Anhydrides may often be obtained from the corresponding acid.

Catalysis.—A chemical change which takes place so slowly under certain conditions of temperature and pressure as to be inappreciable, may take place with immeasurably greater rapidity in presence of some element or compound which itself *seems* to take no part in the given change. Thus, in the case of sulphur dioxide and oxygen, when platinum is absent the gases combine very slowly indeed; but when platinum is present in a suitable form, all other conditions remaining the same, combination occurs rapidly; a small quantity of platinum suffices for the production of a practically unlimited quantity of sulphur trioxide, and yet the metal is unchanged at the end of the process.

Again, the decomposition of potassium chlorate is very much hastened in presence of a relatively small proportion of manganese dioxide, which *seems* to take no part in the reaction, and which is itself unchanged at the end of the process (p. 83).

Substances like these which *accelerate* chemical change are called catalysts, and their action *catalysis.** A substance which serves as a catalyst in a particular reaction may have no effect whatever in other reactions. Water is one of the most important catalysts; many reactions which occur readily in presence of *traces* of water do not take place in its absence to any appreciable extent. Oxygen and hydrogen, for example, do not combine when sparks are passed through an *absolutely dry* mixture of the gases.

SULPHUROUS ACID.

Sulphur dioxide is very soluble in water (its *solubility* at 16° is 4200). When a stream of the gas is led into cold water a slight development of heat occurs, but no other sign of chemical change is observed; the solution has the same smell as the gas, and the gas is completely expelled on boiling. So far, therefore, the process of solution seems to be a physical change.

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* There are some catalysts which *retard* chemical change.

The solution has a sour taste, turns blue litmus red, and acts on a few metals—magnesium, for example—with liberation of *hydrogen*; that is to say, a solution of sulphur dioxide in water is in these respects like a dilute solution of hydrogen sulphate or hydrogen chloride. When sulphur dioxide is passed (in excess) into a solution of lime-water, and the solution is then evaporated on the water-bath, a colourless, crystalline, *odourless* compound is deposited. If this solid is separated, washed with a little water, and then placed in dilute hydrochloric acid, a vigorous effervescence is observed, and sulphur dioxide is evolved; hence this solid contains combined sulphur and oxygen. When some sulphuric acid is poured on to this solid substance, sulphur dioxide is evolved; on heating strongly to expel the *excess* of sulphuric acid, there remains a residue which can be identified as pure calcium sulphate. Hence the solid is a compound of *calcium* as well as of sulphur and oxygen.

Quantitative experiments show that 119·1 units of the solid give 136 units of calcium sulphate. These qualitative and quantitative results correspond with the equation,

$$\underbrace{CaSO_3 + H_2}_{39\cdot7+31\cdot8+47\cdot6}SO_4 = \underbrace{CaSO_4 + H_2}_{39\cdot7+31\cdot8+63\cdot5}O + SO_2$$

The solid compound which is thus shown to be $CaSO_3$ is called **calcium sulphite.**

Now calcium sulphate may be regarded as a compound of the two oxides CaO and SO_3, and calcium sulphite may be similarly regarded as a compound of CaO and SO_2; but calcium sulphate is derived from sulphuric acid, H_2SO_4, by displacing the hydrogen of the acid by the metal calcium,

$$CaO + H_2SO_4 = CaSO_4 + H_2O;$$

and if calcium sulphite is regarded as having been formed in a similar manner from an acid, H_2SO_3,

$$CaO + H_2SO_3 = CaSO_3 + H_2O,$$

then the production of this 'salt' and many other properties of the solution of sulphur dioxide are accounted for.

Therefore, although a compound of the formula H_2SO_3 has never been isolated, it seems probable that this substance is really formed when sulphur dioxide and water are brought together, just as hydrogen sulphate is formed from sulphuric anhydride and water (p. 232),

$$SO_2 + H_2O = H_2SO_3$$
$$SO_3 + H_2O = H_2SO_4.$$

When this view is adopted it is easy to understand why the two solutions are similar in so many of their properties: they contain substances of the same nature or *same type*.

Sulphur dioxide, therefore, is regarded as the *anhydride* of the acid H_2SO_3 (p. 233), and is also called sulphurous anhydride, the acid, H_2SO_3, being known as **sulphurous acid.**

Calcium sulphite and other compounds formed from sulphurous acid in a similar manner are classed together as the *sulphites* (compare p. 260).

Sulphurous acid, or moist sulphur dioxide, is an important 'bleaching' agent. When the acid is added to a solution of 'magenta' the colour of the dye is discharged; violets and other flowers placed in a jar of the moist gas are also bleached. The action of sulphurous acid is milder than that of chlorine, and is also less destructive to the fabric or other material which requires to be 'bleached.' For this reason sulphurous acid is employed in bleaching wool, straw, and other fibrous materials on which chlorine has a harmful effect (compare p. 289).

CHAPTER XXVII.

Nitric Acid and some Compounds obtained from it.

When nitre (saltpetre or *potassium nitrate*) is heated with sulphuric acid (in a retort, fig. 71),* a brown or yellow vapour is evolved at first, and then there distils a brown or yellowish fuming liquid, known as *nitric acid*, which is essentially the same as that obtained by heating a mixture of nitre and green vitriol (p. 39). This liquid has a pungent and characteristic smell, and is extremely corrosive, causing severe wounds or 'burns' if it gets on to the skin.† It also acts violently on sawdust, india-rubber, cork, and most other vegetable as well as animal matter, and on all well-known metals except gold and platinum; for these reasons it was once called *aqua fortis*.

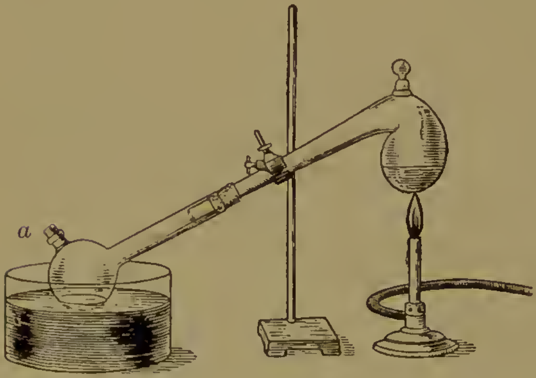

Fig. 71.

Gold, silver, and platinum are not oxidised when they are left exposed to or heated in the air, and for this reason they used to be called 'noble' or 'royal' metals, others being called 'base' metals. Although hydrochloric or nitric acid alone has no action on two of these noble metals (gold and platinum), a *mixture* of the two acids acts readily on both, converting them into soluble yellow chlorides. This mixture of acids, known as *aqua regia*, owes its action to the fact that nitric acid decomposes hydrogen chloride and liberates chlorine. All metals are attacked by—that is to say, combine with—chlorine.

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* The cork (*a*) fits *quite loosely* or a hole is pierced in it.

† Compare footnote, p. 39.

'Nitric acid' is prepared commercially by heating sodium nitrate (Chili saltpetre) with sulphuric acid. When the commercial acid is heated in a distillation apparatus (fig. 7, p. 12) brown or ruddy fumes soon fill the flask and the liquid begins to boil, but the temperature does not remain constant, so that either the 'nitric acid' is a mixture or it decomposes. By fractional distillation under reduced pressure (p. 18)* a colourless liquid of constant boiling-point may be obtained. This substance is **nitric acid**, or *hydrogen nitrate;* its specific gravity is 1·56 at 0°; under atmospheric pressure it boils at 86°, but decomposes to some extent, giving a brown gas. It is miscible with water, and its dilute solution has a sour taste and turns blue litmus red.

Commercial nitric acid contains from 1 to 50 per cent. of water, and is coloured by dissolved gases (p. 246).

Nitric acid is used commercially in the manufacture of sulphuric acid (p. 287) and in the preparation of many explosives (dynamite, gun-cotton, cordite) and many dyes.

Nitric acid attacks copper with great violence; effervescence sets in, a brown gas is seen, the metal disappears, and there remains a blue solution which on evaporation gives blue crystals of copper nitrate (p. 42). When copper nitrate is heated it is decomposed, a brown gas is liberated, and black copper oxide remains (p. 43); hence copper nitrate and nitric acid contain combined *oxygen.*† What other element or elements does nitric acid contain?

Experiments have shown that when nitric acid (which has been most carefully purified) is gently heated and its vapour is passed over strongly heated copper *three* products are formed, namely, copper oxide, water, and nitrogen; hence nitric acid or hydrogen nitrate is a compound of three elements—*hydrogen*, *oxygen*, and *nitrogen* (p. 245).

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* Adding some sulphuric acid, which prevents water from distilling with the nitric acid.

† When mercury is treated with nitric acid it is converted into mercuric nitrate, which when gently heated gives mercuric oxide. It was in this way that the presence of combined oxygen in nitric acid was first proved by Lavoisier.

The percentage composition of nitric acid may be determined by decomposing a weighed quantity of the pure compound in this way with a known weight (excess) of copper, collecting the *water* in a calcium-chloride tube and the dry *nitrogen* over mercury. The percentage of hydrogen is calculated from the weight of the water, that of the nitrogen from its *volume*, that of the *oxygen* from the weight of the water *and* the increase in weight of the copper. The analysis requires special apparatus, as all air and moisture must be excluded, and on this account details are omitted.

As it is very difficult to obtain nitric acid quite free from water, and as the determination of its composition by the analysis of the acid itself is by no means an easy task, the results are not very accurate. It is not necessary, however, to estimate all three elements directly, since either the oxygen *or* the nitrogen may be found *by difference* (p. 125). Further, the estimation of the three elements in *one* operation is also unnecessary, so that conditions suitable for the determination of one constituent only may be chosen; thus one experiment may be made to determine the hydrogen, another to determine the nitrogen, and a third to determine the oxygen.

It is thus found that nitric acid consists of oxygen 76·2, nitrogen 22·2, and hydrogen 1·6 per cent., and its empirical formula, deduced in the usual way, is HNO_3.

$$\left.\begin{array}{ll}\text{Hydrogen,} & 1{\cdot}6 \div 1 = 1{\cdot}6 \\ \text{Nitrogen,} & 22{\cdot}2 \div 14 = 1{\cdot}6 \\ \text{Oxygen,} & 76{\cdot}2 \div 16 = 4{\cdot}8\end{array}\right\} \text{ and } 1{\cdot}6 : 1{\cdot}6 : 4{\cdot}8 \text{ as } 1 : 1 : 3.$$

This formula is confirmed by the results of more accurate analyses of silver nitrate and other derivatives (salts) of nitric acid.

Silver nitrate has been known for a long time, and is a very important compound. Silver is readily acted on by hot dilute nitric acid, a brown gas is seen, and a colourless solution results; on concentrating and cooling, *anhydrous* colourless crystals of silver nitrate are deposited.

The percentage of silver in silver nitrate may be accurately determined by dissolving a weighed quantity of the pure metal in pure diluted nitric acid, evaporating to dryness (and until constant), and weighing the residue of silver nitrate.

5 g. of silver give 7·894 g. of silver nitrate; the percentage of silver in this substance, therefore, is 63·3.

The silver may also be estimated by dissolving a known weight of pure silver nitrate in *distilled* water and precipitating the metal as chloride by adding a slight excess of hydrochloric acid (compare p. 149); the silver chloride is then separated, dried, and weighed.

2·82 g. of silver nitrate give 2·37 g. of silver chloride. The composition of silver chloride is, silver 75·3, and chlorine 24·7 per cent. Hence 2·37 g. of silver chloride contain 1·785 g. of silver. As this is the weight of the silver in 2·82 g. of silver nitrate, the percentage of the metal is $\frac{1{\cdot}785 \times 100}{2{\cdot}82} = 63{\cdot}3$.

Now silver nitrate does not contain any combined hydrogen, and it can be calculated that a substance of the formula $AgNO_3$ would contain 63·3 per cent. of silver.

Since Ag = 107, N = 14, O = 16 (in whole numbers), the molecular weight of $AgNO_3$ would be 169 and $\frac{107 \times 100}{169} = 63{\cdot}3$.

Therefore, as the formula of nitric acid is HNO_3 and silver nitrate is produced from silver and nitric acid, it would seem that the metal displaces hydrogen from the acid, just as metals as a class displace hydrogen from hydrogen chloride and hydrogen sulphate. This conclusion does not at first sight seem to be borne out by a study of the action of nitric acid on metals, for although silver, copper, lead, mercury, zinc, iron, and others dissolve chemically in the acid, hydrogen is not liberated, a different gas (or gases) altogether being set free. This change is described later (p. 245), but the fact may be recalled that metals do not liberate hydrogen from hot concentrated sulphuric acid.

Now when *metallic oxides* are placed in nitric acid they dissolve chemically without any gas being liberated, just as they do in hydrochloric acid and in sulphuric acid. Thus when copper oxide is placed in nitric acid it dissolves chemically, giving a blue solution of copper nitrate; similarly, litharge (lead oxide), mercuric oxide, and magnesium oxide dissolve chemically, and crystalline substances (salts) are obtained on evaporating the solutions. In these reactions double decomposition occurs, and the hydrogen of the nitric acid combines with the oxygen of the metallic oxide, as represented by the following equations,

$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O$$
$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O.$$

The compounds formed in this and in other ways by displacing the hydrogen of nitric acid by metals are classed as salts of the acid and are called *nitrates.*

NITROGEN PENTOXIDE.

When pure nitric acid is very carefully mixed with excess of phosphorus pentoxide (p. 85) and the mixture is gently heated (in a retort), there distils an orange-coloured liquid, from which by cooling in a freezing mixture a colourless crystalline substance (m.p. 30°) may be isolated. This compound boils at 45°, decomposing to some extent; it dissolves chemically in water, with development of heat, and nitric acid is formed. Its formula is N_2O_5, and it is also called *nitric anhydride* because it combines with water and produces an acid (compare p. 233),

$$N_2O_5 + H_2O = 2HNO_3.$$

Phosphorus pentoxide decomposes nitric acid, and combines with the water which is formed.

THE NITRATES.

Since one atom of a univalent element displaces one atom of hydrogen, and one atom of a bivalent element displaces two, and so on, the formula of a *nitrate* is $M(NO_3)$, $M(NO_3)_2$,

$M(NO_3)_3$,* and so on according to the *valency* of the metal represented by M. The group of atoms (NO_3) which is present in all these compounds, and which can be transferred without change from one compound to another, as when silver nitrate is treated with hydrogen chloride,

$$AgNO_3 + HCl = AgCl + HNO_3,$$

is called the nitric acid *radicle* (compare p. 228). This radicle is univalent.

Potassium nitrate, KNO_3 (nitre or saltpetre), has already been mentioned (p. 35), and also **sodium nitrate,** $NaNO_3$ (Chili saltpetre). These two compounds occur naturally in large quantities in hot countries (India, Chili, Peru), which have a long dry season, and the way in which they are formed is very interesting.

Vegetable (and animal) matter, composed of compounds of carbon, hydrogen, oxygen, and nitrogen, decaying in the air, is oxidised in the presence of certain 'nitrifying' bacteria in such a way that nitric acid is formed; the acid then attacks mineral matter and forms a nitrate of sodium, potassium, or calcium. Animal refuse (dung, &c.) is richer in nitrogen compounds than vegetable matter, and is employed in India in the 'artificial' preparation of nitre.

Sodium and potassium nitrates are colourless, crystalline, and readily soluble in water. When they are strongly heated they first melt and then decompose, giving oxygen (compare p. 82) and a substance called a *nitrite*,

$$2KNO_3 = O_2 + 2KNO_2.$$

Potassium nitrate is used in the manufacture of gunpowder (p. 30),† but sodium nitrate is hygroscopic, and therefore could not be employed for such a purpose. Sodium nitrate is used in the manufacture of nitric acid,* and both salts are also employed as manures.

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* Brackets are used in this and in similar cases partly to express the idea of a radicle, partly because the relationship between the three formulæ is clearer than if they were written MNO_3, MN_2O_6, and MN_3O_9 respectively.

† Gunpowder, which is a mixture of potassium nitrate, sulphur, and charcoal in variable proportions, is explosive because when it is heated the sulphur and carbon decompose the potassium nitrate, and a large volume of a mixture of sulphur dioxide, carbon dioxide, and nitrogen is suddenly formed, together with potassium sulphate, carbonate, and other products.

Silver nitrate, $AgNO_3$, has already been referred to (p. 238). It melts at 198°, and is often cast into sticks, but at much higher temperatures it decomposes and gives silver, a brown gas, and oxygen. When rubbed on the skin it produces after some time a black stain, and a sore or 'burn' if applied sufficiently.† Silver nitrate is very poisonous. It is used largely in photography and in the laboratory.

Copper nitrate, $Cu(NO_3)_2$, crystallises with three molecules of water, forming beautiful blue crystals, $Cu(NO_3)_2, 3H_2O$. When strongly heated it decomposes, giving oxygen, a brown gas, and a residue of cupric oxide, CuO.

Lead nitrate, $Pb(NO_3)_2$, may be prepared by chemically dissolving lead or litharge in nitric acid. On the solution being evaporated, the salt is deposited in colourless anhydrous crystals, which when heated strongly *decrepitate* (p. 35) ‡ and decompose, giving oxygen, a brown gas, and a residue of lead oxide, PbO.

These examples illustrate the general behaviour of the nitrates, all of which are decomposed at moderately high temperatures. Some, such as potassium and sodium nitrates, give oxygen and a *nitrite* of the metal; others—and this is the more common behaviour—give a mixture of oxygen and a brown gas (nitrogen tetroxide, p. 246), leaving a residue of the *metallic oxide*. A few—silver nitrate and mercury nitrate, for example—give the gases just named and the *metal*, because the oxides of these metals are themselves decomposed at high temperatures.

A few metallic nitrates are decomposed by water, giving

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* The formation of nitric acid is expressed by the equation,

$$2NaNO_3 + H_2SO_4 = 2HNO_3 + Na_2SO_4.$$

† Silver nitrate was once called 'lunar caustic,' silver itself being known as 'Luna' (the moon), from its bright, shining appearance.

‡ The liberation of gas causes these crystals to break up violently.

insoluble compounds; all the others are soluble in water, and all are soluble in dilute nitric acid.

Some natural waters contain traces of nitrates.

NITRIC OXIDE.

When copper turnings are placed in a Woulff's bottle provided with a thistle funnel, &c., exactly as shown in fig. 19 (p. 63), and nitric acid is poured down the funnel (footnote †, p. 62),* the bottle is rapidly filled with a brown gas, and a gas displaces the water from the cylinder; but the gas in the cylinder is *colourless*, not brown, and after some time the brown gas is no longer seen in the bottle. The cylinder is removed from the beehive and left inverted in the trough, while other jars are filled with the gas and closed with glass plates. The gas does not dissolve in the water to any very appreciable extent; its *solubility* at 15° is about 5.

If the glass plate is now removed from a cylinder of the gas, an extraordinary phenomenon is observed; the gas near the open end of the jar immediately becomes brown. This must be due to some action of one (or more) of the components of the air, but obviously not to aqueous vapour. In order to examine this phenomenon, a cylinder is half-filled with the gas and (possibly after first trying carbon dioxide or nitrogen with no obvious result) a little oxygen is bubbled up into the cylinder; brown fumes are immediately seen, from which fact it must be concluded that the colourless gas combines with free oxygen, or is decomposed by it. But the brown fumes disappear again if the cylinder containing them is left inverted in water; hence the brown gas is readily soluble in water. On more oxygen being bubbled up the brown gas is again formed, and again dissolved; and on repeating this process several times it is seen that instead of the volume of gas increasing by the addition of oxygen, it *diminishes*, until with a little care, namely, when *one* volume of oxygen has been added for every *two* volumes of the gas, the water rises to the top of the cylinder. Experiments of this kind were made by Priestley, who, however, used air instead of oxygen.* He first obtained the colourless gas in 1772, and called it 'nitrous air.' It is now known as **nitric oxide.**

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* The acid is diluted to a specific gravity of 1·2, and the contents of the bottle are kept cool.

Nitric oxide may be used as a test for *free* oxygen; no other gas than oxygen forms a brown gas with it. Further, nitric oxide may be used for measuring the volume of free oxygen in the air (or in other gaseous mixtures), because, since the brown gas is soluble in water, the greatest *diminution* in volume obtainable by the gradual addition of nitric oxide (in presence of water) corresponds with the volume of the free oxygen. Nitric oxide, in fact, was so used by Cavendish, Priestley, and others, and as in those days it was supposed that the composition of the air varied at different seasons, the apparatus which was used for this purpose was called a *eudiometer* (p. 161, from two Greek words meaning *fine weather* and *a measure*).

Nitric oxide does not burn in the air, and a burning candle or burning sulphur or charcoal is extinguished in the gas. When, however, some brightly burning phosphorus is placed in the gas (footnote, p. 84) combustion continues with increased vigour, and a dense white smoke fills the vessel. The white solid thus formed is identical with phosphorus pentoxide (the compound obtained by burning phosphorus in oxygen, p. 85). Nitric oxide, therefore, contains oxygen; it cannot be or contain free oxygen, as it gives a brown gas when it is mixed with oxygen.

When nitric oxide is slowly passed through a glass tube containing a long layer of red-hot copper, the metal is changed into a black substance which can be identified as copper oxide. Some gas escapes, and may be collected over water (as soon as all the air in the tube has been displaced). This gas is invisible, odourless, and practically insoluble in water; it extinguishes all burning substances; when it is dry and pure its density is 14, which is that of the element *nitrogen* (p. 93). Nitric oxide, therefore, is a compound of *nitrogen* and *oxygen.*

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* Priestley wrote afterwards: 'I hardly know any experiment that is more adapted to amaze and surprise than this, which exhibits a quantity of air which as it were devours a quantity of another kind of air half as large as itself, and yet is so far from gaining any addition to its bulk that it is considerably diminished by it.'

Now the density of pure nitric oxide is 15, so that its molecular weight is 30; as its molecule must contain at least one atom of nitrogen (at. wt. 14) and one atom of oxygen (at. wt. 16), its molecular formula is NO.

The nitric oxide obtained by the action of nitric acid on copper is generally mixed with nitrous oxide (p. 268), and the proportion of the latter depends on the concentration of the nitric acid and on the temperature at which interaction occurs. Nitric oxide is absorbed by a solution of ferrous sulphate (green vitriol, p. 226), forming a black soluble compound, which is decomposed on heating its solution, nitric oxide being evolved. These facts may be made use of in separating nitric oxide from nitrous oxide and other gases.

It is obvious that the formation of nitric oxide from nitric acid by the action of copper (and other metals, such as mercury) is not a simple substitution (p. 146), and that both oxygen and hydrogen are removed from some of the HNO_3 molecules. As, at the same time, the copper is changed into $Cu(NO_3)_2$, some of the HNO_3 molecules lose hydrogen only.

It seems probable, therefore, that several distinct changes occur, and that the nitrate is formed in some indirect manner, just as a sulphate is so formed when a metal is heated with concentrated sulphuric acid (compare p. 230).

It may be supposed that the metal, copper, for example, is first converted into oxide by some of the nitric acid, which is thereby decomposed into water and nitric oxide,

$$3Cu + 2HNO_3 = 3CuO + H_2O + 2NO;$$

and that the copper oxide and more nitric acid then form copper nitrate and water,

$$3CuO + 6HNO_3 = 3Cu(NO_3)_2 + 3H_2O.$$

These two reactions being combined, the final result may be expressed by the equation,

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

This view is supported by the fact that some metals—tin, for example—are converted into their *oxides*, and not into their nitrates, by concentrated nitric acid. When this acid is poured on some tin a violent action occurs, a brown gas is seen, and the tin is changed into a white powder, *stannic oxide*, SnO_2, combined with water.

It is also known that nitric acid 'oxidises' many elements besides the metals; thus when sulphur is heated with nitric acid it is changed into sulphur trioxide, which, with the water present, forms sulphuric acid (p. 232). This important property of nitric acid is referred to again (p. 286).

Nitrogen Tetroxide.

The brown gas which is formed when nitric oxide and free oxygen are brought together changes to a pale-yellow liquid (b.p. 22°), and then to an almost colourless crystalline solid (m.p. $-12°$), when it is cooled sufficiently. It can be shown that this solid has the molecular formula N_2O_4, so that it is produced by the *combination* of oxygen and nitric oxide. It is called *nitrogen tetroxide.*

The brown gas in question may be produced in various other ways. It is formed when nitric acid is distilled, a part of the acid being decomposed into brown gas, oxygen, and water; the brown gas dissolves in the distillate, giving it a brown or yellow colour. It is also formed when lead nitrate and several other metallic nitrates are heated (compare p. 242), and, further, by the combination of oxygen and nitrogen.

If a flask containing air, or any *mixture* of oxygen and nitrogen, is fitted up as shown (fig. 72), with two (copper) wires, between which electric sparks can be passed, then, on 'sparking,' the gaseous mixture is locally heated at a very high temperature. After some time the contents of the flask become brown, owing to the formation of nitric oxide, which combines with oxygen, giving nitrogen tetroxide.

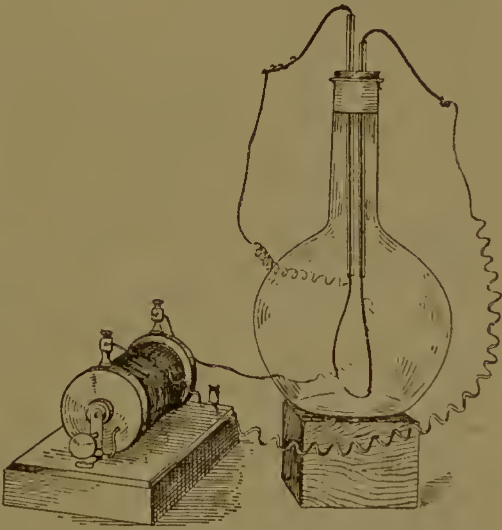

Fig. 72.

Nitric oxide is decomposed into nitrogen and oxygen if it is heated very strongly. When, therefore, the mixture of gases has been sparked for some time, the proportion of tetroxide does not increase but remains constant, because just as much of the oxide is decomposed as is formed in a given time. The reactions are reversible.

This combination of oxygen and nitrogen was studied by Cavendish (in 1784), and he showed that when the brown gas is absorbed in caustic potash (p. 79) the solution, on evaporation, gives crystals of nitre (potassium nitrate).*

Nitrates are now made commercially by 'sparking' air, absorbing the brown gas in water, and then neutralising with calcium carbonate, sodium carbonate, &c. (p. 299).

Small quantities of nitrogen tetroxide are formed during thunderstorms, and carried down to the earth as nitric acid, which then acts on the earthy materials, forming nitrates.

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* The element nitrogen was so named because it gave rise to nitre. It is now known that when the brown gas is dissolved in caustic potash it forms not only potassium nitrate, but also *potassium nitrite* (p. 241), a salt of nitrous acid,

$$N_2O_4 + 2KOH = KNO_3 + KNO_2 + H_2O.$$

The nitrates so formed are absorbed by plants. The combination of nitrogen and oxygen under the influence of the lightning discharge does not continue, because the reaction is endothermic (p. 137).

CHAPTER XXVIII.

Acids, Bases, and Salts.

Acids.—The term 'acid' which is applied to many different compounds is a general or class name like the terms 'metal' and 'salt;' it was originally given to substances which had a sharp or sour taste and a corrosive action on metals, and which turned blue vegetable dyes, such as litmus, into red ones. All the acids which so far have been described show these common properties, but at the same time differ from one another in many respects.

Now when Lavoisier was making experiments on 'burning' or combustion, he noticed that when certain elements such as carbon, sulphur, and phosphorus were burnt in Priestley's 'dephlogisticated air' and the products of combustion were afterwards dissolved in water, the resulting solutions had the properties of acids. Hence he concluded that an element formed an acid when it combined with 'dephlogisticated air,' and the name *oxygen* which he then gave to this 'air' means *acid-producer.* Many oxides, such as carbon dioxide, sulphur dioxide, and phosphorus pentoxide (p. 85), were therefore regarded as acids; but later on, when the composition of hydrogen chloride was established,* it was recognised that a substance which does not contain oxygen may yet be an 'acid.' In the course of time it was found that **acids** are always compounds of *hydrogen*, and that those oxides which give acids when they are dissolved in water become acids only after they have *combined* with (the elements of) water and been changed into compounds of hydrogen, as well as of oxygen.

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* For some time it was supposed that hydrogen chloride contained combined oxygen, because its solution in water had the properties of an acid, and chlorine was regarded as a *compound* of oxygen with some unknown element or elements.

Thus carbon dioxide, sulphur dioxide, and phosphorus pentoxide are not acids themselves, but when brought into contact with water they *combine* with it, and *carbonic*, *sulphurous*, or *phosphoric acid*, as the case may be, is thus produced.

As a result of this combination both the *oxide* and the *water*, as such, no longer exist; their molecules are changed; and a new compound, having totally different properties, is formed. This is not obvious in the cases of carbon dioxide and sulphur dioxide; these gaseous oxides dissolve in water (chemically) without outward sign of chemical change, in much the same way, apparently, as does oxygen or hydrogen, and they are expelled again, as oxides, on the solutions being heated. Nevertheless, although most of the water (which is present in great excess) remains unchanged, and merely acts as a solvent, the aqueous solutions doubtless contain definite compounds, H_2CO_3 and H_2SO_3 respectively, and it is only because these compounds are easily decomposed that they cannot be isolated—that is to say, obtained free from water.

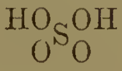
Facts have already been given which seem to prove the existence of sulphurous acid, H_2SO_3 (p. 233); and similar evidence is given later in the case of carbonic acid, H_2CO_3 (p. 271). That many oxides (anhydrides) *combine* with water during solution to produce acids may, however, be proved by direct evidence; thus sulphuric acid and nitric acid may be obtained by the combination of the respective anhydrides with water,

$$SO_3 + H_2O = H_2SO_4$$
$$N_2O_5 + H_2O = 2HNO_3.$$

Hence it is hardly true to say that oxides such as these dissolve in water; it is the *products* which pass into solution and which are the *acids*.

The analysis of these acids has shown that their formation is expressed by the above equations; their chemical examination has led to the conclusion that each of the hydrogen atoms in their molecules is held by, attracted by, or combined with one particular oxygen atom; this may be indicated by writing their formulæ $SO_2(OH)_2$ and $NO_2(OH)$ respectively.

The group or radicle (p. 228), namely (OH), which is thus contained in these molecules is called the *hydroxyl*-group, and a compound which contains one or more hydroxyl-groups is called a **hydroxide.**

The use of formulæ such as $SO_2(OH)_2$ and $NO_2(OH)$ is of some help in forming a mental picture of chemical change. In every molecule composed of two or more atoms, the atoms are held together and can only be separated by the application of heat or other form of energy; they attract one another with some power or force which is often called chemical affinity. Owing to the attractions of the different elements for one another, the atoms in the molecules become arranged or grouped in some definite manner, so that the molecule may be regarded as a *structure* of definite form. Thus the molecule of sulphur trioxide may be pictured as a structure in which one atom of sulphur is attracting three atoms of oxygen, thus $O\underset{O}{S}O$, and that of water as a structure in which one atom of oxygen is attracting two atoms of hydrogen, thus HOH. When a molecule of sulphur trioxide combines with a molecule of water, the atoms rearrange themselves and a totally new structure or molecule is formed, namely, that of sulphuric acid,  $\begin{array}{c}HO\,S\,OH\\ O\quad O\end{array}$ or $O_2S(OH)_2$ or $SO_2(OH)_2$, in which each of the hydrogen atoms is held or attracted by one particular oxygen atom, forming a hydroxyl-group.

Formulæ of this kind (*constitutional formulæ*) may serve to recall the fact that although sulphuric acid is produced by the combination of one molecule of sulphur trioxide with one molecule of water, the molecule of the acid itself contains neither of these molecules, but is a new and distinct structure, different from both.

A radicle (p. 228) is thus to be regarded as a portion of a structure, or molecule, which occurs in the molecules of many different compounds.

Although the hydroxides of many elements are acids, an acid is not always a hydroxide. Hydrogen chloride and hydrogen sulphide are acids, but not hydroxides; water, on the other hand, is a hydroxide, but not an acid.

Hence it is not the mere presence of combined hydrogen which causes a substance to have acid properties; such properties are only shown by compounds in which the hydrogen is combined with particular elements or in a particular way. The hydrogen compounds of chlorine and of sulphur are acids; those of oxygen and of carbon, for example, are not.

It is also noteworthy that although the hydrogen compounds of oxygen and of carbon are not acids, yet many acids are known which consist only of the three elements hydrogen, oxygen, and carbon, as, for example, carbonic acid (p. 271) and acetic acid (p. 277). From such facts it must be concluded that the properties of a substance depend not only on the nature (or kind) of the atoms which it contains, but also on how they are arranged together to form the molecule.

Basic hydroxides.—The compound quicklime or calcium oxide combines with water to form calcium hydroxide (p. 71); here again it is known that both the metallic oxide and the water are changed, and the result may be expressed thus,

$$CaO + H_2O = Ca(OH)_2.$$

Although calcium hydroxide is thus produced from an oxide by a process similar to that by which sulphuric, nitric, and other acids are formed from their respective anhydrides, it differs from the acids in a marked manner. It has not a sour taste, does not corrode metals, and does not change blue, to red, litmus; but litmus which has been turned red by an acid becomes blue again when calcium hydroxide is added to it.

Now calcium hydroxide is readily acted on by acids; thus with hydrochloric, nitric, sulphurous, and sulphuric acids it yields, in addition to water, a *salt*—that is to say, a compound which is formed from the acid by the displacement of its hydrogen by a metal,

$$\begin{aligned}&Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O\\&Ca(OH)_2 + 2HNO_3 = Ca(NO_3)_2 + 2H_2O\\&Ca(OH)_2 + H_2SO_3 = CaSO_3 + 2H_2O\\&Ca(OH)_2 + H_2SO_4 = CaSO_4 + 2H_2O.\end{aligned}$$

The properties of salts are very different from those of the compounds from which they have been formed; thus, compared with the highly corrosive acids, they may be regarded as mild or *neutral* substances, and even when compared with calcium hydroxide, they seem to be very passive; for example, they do not as a rule change the colour of either red or blue litmus.

Many hydroxides resemble calcium hydroxide inasmuch as they act on and 'neutralise' acids, a *salt* and water being formed; such hydroxides are called *basic hydroxides* or *bases*,* and the oxides from which they are produced are called *basic oxides*.

Thus copper hydroxide, lead hydroxide, and silver hydroxide are basic hydroxides, and their behaviour towards acids is expressed by equations such as the following,

$$\begin{aligned}&Cu(OH)_2 + H_2SO_4 = CuSO_4 + 2H_2O\\&Pb(OH)_2 + 2HNO_3 = Pb(NO_3)_2 + 2H_2O\\&Ag(OH) + HCl = AgCl + H_2O.\end{aligned}$$

The oxides CuO, PbO, and Ag_2O respectively, obtained by heating these hydroxides, are basic oxides.

Some basic hydroxides, such as sodium hydroxide, NaOH, and potassium hydroxide (pp. 78, 79), which are readily soluble in water, are extremely active substances, and such very active hydroxides are called *alkalis*.

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* Most of the common 'mineral' acids are liquids (nitric and sulphuric acids) or solutions (hydrochloric acid), and leave no residue when sufficiently heated; when treated with solid, non-volatile calcium hydroxide they give solid, non-volatile products, which seem to owe their solidity to a foundation or *base* of calcium hydroxide.

Salts.—A salt may therefore be regarded from several standpoints: as a compound formed, *together with water*, by the interaction of an acid and a basic hydroxide, or by the interaction of an acid and a basic oxide,

$$Ag_2O + 2HCl = 2AgCl + H_2O\,;$$

also, as a compound formed by displacing the hydrogen of an acid by a metal (compare pp. 146, 147, 224, 239).

The meanings of the terms just referred to may be further illustrated by considering the behaviour of two widely different elements, sodium and sulphur. *Sodium* is a lustrous solid, not unlike silver in appearance, but much more active chemically; when placed in water it liberates hydrogen at ordinary temperatures (p. 107), and there is formed a solution of a colourless crystalline substance, sodium hydroxide,

$$2Na + 2H_2O = 2Na(OH) + H_2,$$

identical with that formed from sodium carbonate and calcium hydroxide (p. 78). Sodium hydroxide is also formed when sodium oxide is placed in water,

$$Na_2O + H_2O = 2Na(OH)\,;$$

it is a very active substance, is caustic, and turns red litmus blue.

Sulphur does not act on water; it combines with oxygen and forms two oxides (anhydrides), both of which unite with water. The hydroxides thus formed, namely, sulphurous and sulphuric acids, have a sour taste, corrode metals, and turn blue litmus red.

When a little litmus solution is added to one of these acids, say sulphuric acid, and a solution of sodium hydroxide is then slowly dropped in (from a burette), the red colour of the solution changes to blue where the drops fall, but on the solution being shaken, the blue colour immediately gives place to red. As the addition of the sodium hydroxide solution is continued, the blue colour changes more and more slowly, until at last with careful work the whole of the solution is coloured neither blue nor bright red, but an intermediate 'port-wine' shade. The solution now does not contain either sulphuric acid or sodium hydroxide, and when evaporated it yields crystals of *sodium sulphate* (p. 226), a substance which does not change the colour of blue or red litmus, which is neither caustic nor sour, and which, compared with sodium hydroxide or with sulphuric acid, may be regarded as an extremely mild or neutral substance. The sodium hydroxide and sulphuric acid are said to have *neutralised* one another; they have been mixed in *equivalent* quantities and have formed a *salt* and water,

$$2Na(OH) + H_2SO_4 = Na_2SO_4 + 2H_2O.$$

Many compounds behave like sulphuric acid towards sodium hydroxide, and are classed as *acids;* all such compounds contain combined *hydrogen;* many of them are formed by the union of an oxide with water; such oxides are called *anhydrides* or *acid-forming oxides;* elements which give rise to acid-forming oxides *only* are called *non-metals.*

An acid the molecule of which contains *one* atom of hydrogen *displaceable by a metal* is called a *monobasic* acid, as, for example, hydrogen chloride and hydrogen nitrate; when there are two atoms of displaceable hydrogen in the molecule, as, for example, in sulphurous and sulphuric acids, the acid is called *dibasic;* if three (as in phosphoric acid, H_3PO_4), the acid is *tribasic;* and so on.

Many hydroxides behave like sodium hydroxide towards acids, and are classed as *basic hydroxides;* all such compounds may be considered as having been formed by the combination of an oxide with water; such oxides are called *basic oxides;* elements which give rise to at least one basic oxide are called *metals.*

A basic hydroxide such as sodium hydroxide or silver hydroxide, the molecule of which contains one hydroxyl-group, is called a *monacid* hydroxide; if two hydroxyl-groups are present in the molecule, as in the hydroxides of lead, copper, and calcium (p. 252), the compound is a *diacid* hydroxide; and so on.

Many basic oxides are insoluble in, and do not combine with, water when they are merely added to it, but the corresponding basic hydroxides may be obtained by other methods.

A basic hydroxide may also be regarded as a compound derived from *water* by the displacement of one atom of hydrogen by an equivalent of a *metal*; thus the univalent metal sodium displaces one atom of hydrogen, forming $Na(OH)$; the bivalent elements calcium, copper, lead, &c. displace two atoms of hydrogen from *two* molecules of water, forming compounds such as $Ca(OH)_2$, $Cu(OH)_2$; and so on. It must not be supposed, however, that all basic hydroxides can be prepared by treating a metal with water; some metals only act on water at high temperatures, while others, such as copper, have no action.

The term '**metal**,' of which some explanation was given very early (p. 35), is applied to a class of elements which have not only certain *physical* but also certain *chemical* properties in common. A metal forms at least one basic oxide, and displaces hydrogen from acids.

The division of the elements into metals and non-metals, of their oxides into basic oxides and acid-forming oxides (anhydrides), and of their hydroxides into bases and acids, is convenient in many ways, and as regards most elements, oxides, and hydroxides, there is not much difficulty in deciding in which of the two classes a given substance should be placed; but in chemistry there are no boundary lines. Some elements, some oxides, and some hydroxides seem to belong to the one class or to the other according to the test which is applied; thus the hydroxide of the element aluminium (p. 295) behaves as a *basic* hydroxide when it is treated with sulphuric acid, but as an *acid* when it is treated with sodium hydroxide, a salt and water being formed in both cases. Further examples will be given later; at this stage it is sufficient to point out that the *exact* definition of terms such as 'acid,' 'base,' &c. is not a simple matter.

TITRATION—VOLUMETRIC ANALYSIS.

In the formation of a salt and water from an acid and a basic hydroxide, an atom of hydrogen from the molecule of the acid combines with a hydroxyl-group from the molecule of the basic hydroxide to form water; it follows, therefore, that *one* molecule of a monobasic acid is equivalent to or neutralises *one* molecule of a monacid hydroxide, that *one* molecule of a dibasic acid neutralises *two* molecules of a monacid hydroxide, that *two* molecules of a monobasic acid neutralise *one* molecule of a diacid base, and so on.

$$HCl + NaOH = NaCl + H_2O$$
$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$$
$$2HCl + Ca(OH)_2 = CaCl_2 + 2H_2O.$$

The relative quantities of acid and basic hydroxide which thus neutralise one another, and which are expressed by the above equations, are thus *equivalent* weights (p. 176).

Now suppose that a solution of hydrogen chloride is gradually added (from a burette, fig. 73) to a solution of sodium hydroxide coloured with litmus until the colour of the solution is neither blue nor red (compare p. 253), the acid and the sodium hydroxide have then been mixed in equivalent quantities, and the solution contains only sodium chloride.

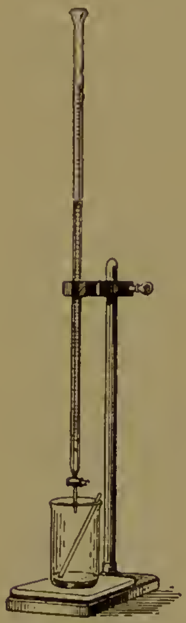
Fig. 73.

If the *weight* of hydrogen chloride in a given *volume* (say 1 litre) of the hydrochloric acid is known, and also the *volume* of the solution which has been run from the burette, the *weight* of sodium hydroxide originally present in the alkaline solution is easily calculated.

Example.—1 litre of the acid contains 36·2 g. of hydrogen chloride; 20 c.c. were used. From the above equation 36·2 g. of HCl are equivalent to 40 g. NaOH. 20 c.c. of the acid contain $\frac{36 \cdot 2 \times 20}{1000} = 0 \cdot 724$ g. HCl. By proportion, therefore, the weight of sodium hydroxide is $\frac{0 \cdot 724 \times 40}{36 \cdot 2} = 0 \cdot 8$ g. in the given solution.

In an exactly similar manner the weight of hydrogen chloride (or other *acid*) may be ascertained with the aid of a solution of sodium hydroxide of known concentration, using litmus as indicator; it is of no consequence whether the acid is added from a burette to a known volume of the sodium hydroxide or *vice versâ*, as when the neutral tint is reached, the substances have been mixed in equivalent proportions.

This operation of estimating the quantity of one substance in a solution, by gradually adding a solution of another substance of *known* concentration until a certain known change occurs, is termed *titration;* the litmus or other substance which shows when the desired change has taken place is termed the *indicator.*

For practical purposes, and to save trouble in calculating the results, the prepared solutions of acids and basic hydroxides used in titrations are generally of a fixed concentration, and are termed *standard* solutions. The quantity of a substance in a given volume (say 1 litre) of its solution is also so chosen that a given volume of any acid neutralises an equal volume of any basic hydroxide; that is to say, all the solutions are of *equivalent* concentration.

The usual standard concentration is 1 gram-molecule (p. 197) of a monobasic acid or monacid base in 1 litre; since 1 molecule of a dibasic acid is equivalent to 2 molecules of a monacid base, the equivalent solution of such an acid contains $\frac{1}{2}$ gram-molecule per litre, and similarly with a solution of a diacid base; in the case of a tribasic acid $\frac{1}{3}$ gram-molecule would be the equivalent quantity. Such solutions are termed *normal* or N-solutions. It is generally convenient to prepare standard solutions of one-tenth of this concentration for more accurate work; these are *deci-normal* or $\frac{N}{10}$ solutions.

ACID SALTS.

When sulphuric acid is added to sodium chloride until the evolution of hydrogen chloride ceases, even on warming gently (as in preparing hydrogen chloride, p. 142), the product crystallises on cooling; if this crystalline mass is crushed, and drained on porous earthenware to get rid of sulphuric acid, and then recrystallised from hot water, colourless 'prisms' of a substance called **sodium hydrogen sulphate** are obtained.

When a measured volume of sodium hydroxide is *neutralised* with (diluted) sulphuric acid as already described, and an equal volume of the same (diluted) acid is afterwards added, then on evaporation, instead of hydrated crystals of sodium sulphate, $Na_2SO_4, 10H_2O$ (p. 226), only long prisms of *sodium hydrogen sulphate* are obtained, and no other substance is mixed with them.

Further, when some hydrated sodium sulphate is dissolved in water and treated with about one-third of its weight of sulphuric acid, the solution on evaporation gives prisms of *sodium hydrogen sulphate.*

The crystals of sodium hydrogen sulphate obtained by these three methods are readily soluble in water, and even after repeated recrystallisation (to remove every trace of sulphuric acid) their aqueous solution has a strong 'acid reaction' to litmus, and dissolves zinc, magnesium, and other metals chemically, with liberation of hydrogen; the solution, in fact, behaves very like a solution of sulphuric acid.

When dry sodium hydrogen sulphate is strongly heated it gives off 'fumes,' and when these are passed into water a solution of sulphuric acid is obtained; the non-volatile residue consists of *anhydrous* sodium sulphate, and if crystallised from water it gives the pure *hydrated* salt, $Na_2SO_4, 10H_2O$.

Quantitative experiments show that the loss in weight observed on heating sodium hydrogen sulphate corresponds with the loss which should occur if the change were expressed by the equation,

$$Na_2SO_4, H_2SO_4 = \underset{\text{(Residue)}}{Na_2SO_4} + \underset{\text{(Volatile)}}{H_2SO_4};$$

and the weight of barium sulphate which is obtained from a given weight of sodium hydrogen sulphate by precipitation with barium chloride (p. 227) corresponds with that calculated from the equation,

$$Na_2SO_4, H_2SO_4 + 2BaCl_2 = 2BaSO_4 + 2NaCl + 2HCl.$$

These facts show that the composition of sodium hydrogen sulphate may be expressed by the formula,

$$Na_2SO_4, H_2SO_4 \text{ or } Na_2H_2(SO_4)_2 \text{ or } NaHSO_4.$$

For many reasons, which it is unnecessary to particularise, the last of these formulæ is used to represent sodium hydrogen sulphate; the substance is regarded as a *salt*, produced by displacing a part of the hydrogen of the acid by the metal. Its formation by the action of sulphuric acid on (1) sodium chloride, (2) sodium hydroxide, (3) sodium sulphate is expressed thus:

$$(1)\ H_2SO_4 + NaCl = NaHSO_4 + HCl.$$
$$(2)\ H_2SO_4 + NaOH = NaHSO_4 + H_2O.^*$$
$$(3)\ H_2SO_4 + Na_2SO_4 = 2NaHSO_4.$$

The molecule of this salt, however, still contains one of the *hydrogen* atoms of the *acid*, and this atom may be displaced by a metal,

$$NaHSO_4 + NaOH = Na_2SO_4 + H_2O.$$

---

* In making sodium hydrogen sulphate, *equivalent* quantities of sodium hydroxide and sulphuric acid are 40 and 98 respectively as expressed by this equation, but in making sodium sulphate, Na_2SO_4, equivalent quantities are 40 × 2 and 98 respectively. The equivalent of a compound, like that of an element, depends on the nature of the chemical change in which it takes part.

Many salts of such a type are known—that is to say, salts formed by displacing only a part of the displaceable hydrogen * of the molecule of an acid; such compounds are named *acid* or *hydrogen* salts in order to distinguish them from those which are produced by displacing the whole of the displaceable hydrogen, and which are called *normal* salts.

Although sodium hydrogen sulphate has an acid reaction to litmus, this is by no means a characteristic property of acid or hydrogen salts as a class; in fact, some of them turn red litmus blue.

Sodium hydrogen sulphite, $NaHSO_3$, is formed when *excess* of sulphur dioxide is passed into a solution of sodium hydroxide,

$$NaOH + H_2SO_3 = NaHSO_3 + H_2O;$$

it is crystalline and readily soluble in water, but when its aqueous solution is boiled the hydrogen salt is decomposed, giving sulphur dioxide (which escapes) and normal *sodium sulphite*,

$$2NaHSO_3 = SO_2 + H_2O + Na_2SO_3.$$

Some of the best-known and most important acid or hydrogen salts are derived from carbonic acid, and are described later.

CHAPTER XXIX.

Ammonia.

A colourless, crystalline substance called *sal-ammoniac* has been known from very early times. Possibly it was first found as a deposit in the neighbourhood of volcanoes; later on it was prepared by extracting with water the soot obtained by burning camel's dung. In more recent times *animal* refuse such as horns, bones, &c. was submitted to destructive distillation (p. 114), and the aqueous distillate was evaporated with hydrochloric acid; the product was crude sal-ammoniac.

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* Some acids contain one or more hydrogen atoms which are never displaced by metals (compare p. 278). The basicity of an acid depends on its *displaceable* hydrogen, and not on the total number of hydrogen atoms in its molecule.

When sal-ammoniac is heated gently dense white 'fumes' are formed. The solid changes into a vapour which condenses directly to the solid again, without passing through the liquid state (sublimation, p. 19). Sal-ammoniac, therefore, may be called a *volatile* substance, and may be separated from non-volatile impurities by *sublimation*.

When sal-ammoniac is mixed with slaked lime a very pungent and characteristic smell is immediately observed, owing to the liberation of an invisible gas called **ammonia**.

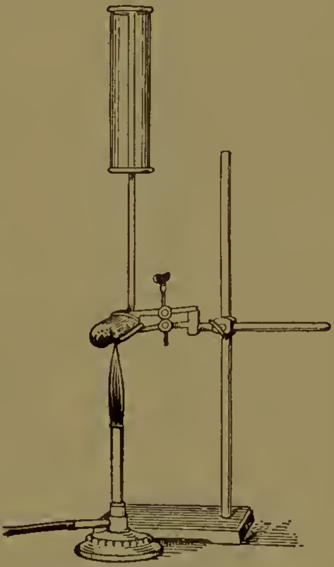

Fig. 74.

Ammonia is prepared by heating a mixture of sal-ammoniac (1 part) and quicklime (1 part) in an angle-tube (fig. 74). As the gas cannot be collected over water, because it is so soluble, it is collected over mercury; or, as it is lighter than air, by displacing air downwards (compare p. 66), as shown. Ammonia is absorbed by the three substances commonly used for drying gases (p. 67), and if required free from aqueous vapour it is passed through tubes containing quicklime, $CaO + H_2O = Ca(OH)_2$.

The great solubility of the gas in water is easily proved by passing up a little water into some of the gas confined over mercury. If the ammonia is free from air and enough water is used, the whole of the gas is immediately dissolved. Its solubility is greater than that of any other gas, *one* volume of water at 15° dissolving 802 volumes of ammonia, and during the solution of the gas a development of heat occurs.

The aqueous solution of ammonia, at one time called *spirit of hartshorn*, has the pungent odour of the gas. When a concentrated solution is heated the gas escapes, together with very little aqueous vapour, and the solution becomes more *dilute*, until finally, after it has boiled for some time, all the ammonia is expelled. The aqueous solution is a commercial product (p. 267), and contains about 36 per cent. of ammonia, its specific gravity being about 0·88. Ammonia is conveniently obtained in the laboratory by *gently* heating this aqueous solution and passing the gas through a vessel (*c*, fig. 75) containing quicklime to dry it.

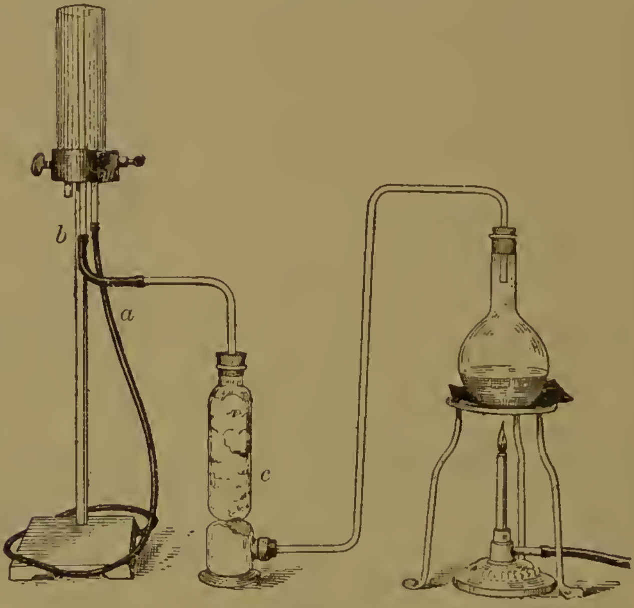

Fig. 75.

Ammonia is non-inflammable under ordinary conditions, and extinguishes a lighted taper and other ordinary flames; in an atmosphere of oxygen, however, ammonia burns with a yellowish, green-edged flame. This can be shown by passing a stream of oxygen through the tube (*a*, fig. 75) and a stream of ammonia through the tube (*b*), and applying a light to the latter. A mixture of oxygen and ammonia in suitable proportions explodes violently when ignited.

A flame of *dry* ammonia burning in dry oxygen deposits a liquid on a cold vessel held in it, and with the aid of a cooling apparatus similar to that used in burning hydrogen (p. 104), a sufficient quantity of this liquid can be collected and identified as *water*. Ammonia, therefore, is a *compound* of hydrogen. If it contained only 1 per cent. of free hydrogen it would not be completely soluble even in fifty times its own volume of water.

The presence of combined hydrogen in ammonia is also shown by passing a stream of the dry gas through a tube containing heated copper oxide; water is formed, and a colourless invisible gas, which can be identified as the pure element *nitrogen*, is liberated; hence ammonia is a compound of nitrogen and hydrogen.

In this experiment dry ammonia is passed through the *cold* tube containing the copper oxide, until all the air is expelled; the oxide is then heated, and after a short time the escaping gas is collected over mercury. A little dilute sulphuric acid floats on the mercury in the gas cylinder so that any unchanged ammonia may be absorbed (p. 266). In order to prove that the gas so obtained is nitrogen, it may be 'sparked' with oxygen (p. 247); but to prove that it is *pure* nitrogen the density of the dry gas may be determined.

A quantitative analysis of ammonia may also be based on this reaction. An unknown weight or volume of the gas is passed very slowly over heated copper oxide, and the nitrogen is collected; from the volume of this gas, the *weight* of the nitrogen is calculated, the weight of the hydrogen being found from the loss in weight of the copper oxide tube. The *relative* weights of the gases in the unknown weight of ammonia are thus found to be, hydrogen 1, nitrogen 4·6. As the atomic weight of nitrogen is 14, the weight of hydrogen which is combined with 14 units or

1 atom of nitrogen is $\frac{14 \times 1}{4 \cdot 6} = 3$ units or 3 atoms; hence the empirical formula of ammonia is NH_3. Now the density of ammonia is 8·5, so that its molecular weight is 17, which corresponds with the *molecular formula* NH_3.

Ammonia, like hydrogen sulphide, is decomposed into its elements when it is strongly heated. When some of the dry gas (say 30 c.c.) confined over mercury (in the apparatus, fig. 60, p. 162) is 'sparked' during some hours, its volume slowly *increases* (say to 40 c.c.); if, then, the volume of the unchanged ammonia is measured by admitting a few drops of dilute sulphuric acid and noting the contraction (say 20 c.c.) which occurs, it is found that the ammonia which has been decomposed (10 c.c.) has given 20 c.c. or twice its volume of gas. This is a mixture of 5 c.c. of nitrogen and 15 c.c. of hydrogen.*

This volume relationship is expressed by the equation,

$$\begin{array}{l} 2NH_3 = N_2 + 3H_2 \\ 2 \text{ vols.} = 1 \text{ vol.} + 3 \text{ vols.}, \end{array}$$

and such a qualitative and quantitative result could not be obtained except with a compound of the molecular formula NH_3.

Although ammonia is a compound of hydrogen, its solution in water is not an acid, but has different properties altogether; it has a soapy feel, and turns red litmus blue, just as does a solution of sodium hydroxide (p. 253) and other strongly basic hydroxides. The substance in solution, therefore, is classed as an alkali (pp. 79, 253).

Now, when an aqueous solution of ammonia is neutralised with hydrochloric acid, using litmus as indicator (p. 257), and then evaporated, crystals of the neutral odourless compound, sal-ammoniac or **ammonium chloride**, are obtained.

As ammonium chloride does not volatilise with water vapour, whereas aqueous solutions of ammonia or of hydrogen chloride leave no residue on evaporation, it does not matter whether the hydrochloric acid is added in excess or not; in either case pure ammonium chloride remains on evaporating to dryness, the excess of ammonia or of hydrogen chloride passing away. If, therefore, *pure* ammonium chloride is required an indicator is not used, and the *dilute* solution of ammonia is merely added to the *dilute* acid until the latter smells faintly of ammonia.

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* The composition of this mixture is determined by exploding it with oxygen.

Ammonium chloride is also formed when ammonia and hydrogen chloride are brought together. If two gas-jars containing the roughly dried gases and closed with glass plates are brought mouth to mouth and the plates are then removed, dense white fumes are formed, with development of heat, and these settle as a crystalline layer on the sides of the jars. If equal volumes of the two gases are brought together over mercury no gas remains, and ammonium chloride is the only product; hence ammonium chloride is formed by the combination of equal numbers of molecules of ammonia and hydrogen chloride,

$$NH_3 + HCl = NH_4Cl.$$

Ammonium chloride gives a precipitate of silver chloride when it is added to a solution of silver nitrate. The combined chlorine in the pure compound can thus be estimated (p. 152), and is found to be 66·0 per cent., a result which corresponds with the above formula.

All chlorides hitherto described may be regarded as salts derived from hydrogen chloride by displacing its hydrogen by an equivalent of some metal, and one method of preparing such chlorides is to treat a basic hydroxide with hydrochloric acid,

$$Na(OH) + HCl = NaCl + H_2O$$
$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O.$$

Now, if ammonium chloride is also to be regarded as a salt derived from hydrogen chloride, the atom of hydrogen must have been displaced by the *group* of atoms (NH_4). The fact that an aqueous solution of ammonia, like that of sodium hydroxide and other basic hydroxides, has an alkaline reaction seems to show that the ammonia has *combined* with the water to form a basic hydroxide, $NH_4(OH)$,

$$NH_3 + H_2O = NH_4(OH).$$

As such a compound has never been obtained from the solution, it may also be supposed that it is *unstable*, and decomposes into ammonia and water when its solution is evaporated. That such a compound actually exists in the solution, however, is probable from a study of its derivatives, just as in the case of sulphurous acid (p. 233) and carbonic acid (p. 271), and it is called **ammonium hydroxide.**

The group of atoms (NH_4) which is contained in ammonium hydroxide, ammonium chloride, and many other compounds is known as the *ammonium radicle.* As this radicle displaces hydrogen from acids it is a *basic radicle*, and as it displaces or is equivalent to one atom of hydrogen it is a univalent radicle. The radicle ammonium, in fact, corresponds in many ways with a single atom of sodium,

$$\begin{array}{ccc} NH_4(OH) & NH_4Cl & (NH_4)_2SO_4 \\ Na(OH) & NaCl & Na_2SO_4, \end{array}$$

and ammonium chloride and other compounds which may be regarded as derived from acids by displacing their hydrogen by (NH_4) are called *ammonium salts.*

Ammonium sulphate, $(NH_4)_2SO_4$, is obtained in colourless crystals when *dilute* sulphuric acid is neutralised with a *dilute* solution of ammonium hydroxide, and the liquid is then evaporated,

$$H_2SO_4 + 2NH_4(OH) = (NH_4)_2SO_4 + 2H_2O.$$

The reaction may be regarded as chemically similar to that which occurs when sulphuric acid is neutralised with sodium hydroxide (p. 254).

In preparing ammonium sulphate in this way the ammonium hydroxide is added in slight excess (until the solution smells of ammonia). On evaporating, any excess of ammonium hydroxide is volatilised, whereas if excess of sulphuric acid were used this compound would not escape with the steam, and the product would be impure.

Ammonium sulphate is prepared in large quantities from gas-liquor (p. 118), which is the principal source of ammonia and its salts. This yellow, watery fluid, obtained in the manufacture of coal-gas, is an aqueous solution of many compounds, of which the more important are ammonium sulphide and ammonium carbonate (p. 276). Coal, like most vegetable and animal matter, contains compounds of nitrogen and of sulphur, and during the highly complex process of destructive distillation ammonia and hydrogen sulphide are produced in small quantities. The 'liquor' is boiled with milk of lime, which decomposes all the ammonium salts present,

$$(NH_4)_2S + Ca(OH)_2 = 2NH_3 + CaS + 2H_2O$$
$$(NH_4)_2CO_3 + Ca(OH)_2 = 2NH_3 + CaCO_3 + 2H_2O,$$

and the ammonia which escapes is passed into an acid in order to obtain the desired salt, or into water if ammonium hydroxide solution is required.

The ammonium sulphate manufactured in this way is largely used as a manure to supply crops (especially the sugar-beet) with the nitrogen compounds which are essential to their growth (p. 139).

Ammonium nitrate, $(NH_4)NO_3$, is formed when *dilute* nitric acid is neutralised with ammonium hydroxide and the solution evaporated; it is colourless and crystalline.

Ammonium sulphide is formed when hydrogen sulphide is passed into a solution of ammonium hydroxide,

$$SH_2 + 2NH_4(OH) = (NH_4)_2S + 2H_2O\,;$$

but if the stream of gas is continued, the *normal* sulphide is converted into *ammonium hydro(gen)-sulphide*,

$$SH_2 + (NH_4)_2S = 2(NH_4)SH.$$

Solutions of these salts are used in the laboratory; when they are evaporated they leave no residue.

All ammonium salts are soluble in water, and many of them sublime when they are heated, leaving no residue, but ammonium nitrate is completely decomposed (p. 268).

Ammonia (or ammonium hydroxide) is sometimes called a volatile alkali in distinction to the non-volatile or 'fixed alkalis,' such as sodium hydroxide.

When any ammonium salt is heated with sodium hydroxide, calcium hydroxide, or other 'fixed' basic hydroxide, ammonia is liberated, and may be identified by its smell and by its action on a red litmus paper.

The quantity of ammonium hydroxide (or of ammonia) in an aqueous solution is easily estimated by titrating with a standard solution of an acid (p. 256). As all ammonium salts are decomposed by sodium hydroxide, the quantity of any known ammonium salt in a given sample (or solution) may be estimated by heating a weighed (or measured) quantity with excess of sodium hydroxide, passing the evolved ammonia into a known volume of standard acid, and then finding the excess of acid (the quantity which has not been neutralised) by titrating with standard alkali.

Example.—0·35 g. of a sample of impure ammonium chloride was heated with excess of sodium hydroxide solution, and the evolved gas passed into 100 c.c. of $\frac{N}{10}$ sulphuric acid. 34·8 c.c. of $\frac{N}{10}$ sodium hydroxide solution were required for neutralisation. Hence 65·2 c.c. of acid had been neutralised by ammonia. 1 c.c. of $\frac{N}{10}$ $H_2SO_4 = 0{\cdot}0049$ g. $H_2SO_4 = 0{\cdot}0017$ g. NH_3; therefore the weight of NH_3 evolved was $65{\cdot}2 \times 0{\cdot}0017 = 0{\cdot}1108$ g., and the percentage of ammonia in the salt 31·7.

NITROUS OXIDE.

When ammonium nitrate is gently heated it first melts and then begins to effervesce, and finally disappears completely. If some of this salt * is *cautiously* heated in a flask provided with a delivery-tube, a colourless (and therefore invisible) gas may be collected by displacement over *hot* water; it is rather readily soluble in cold water (its *solubility* at 15° is 78), but, as is the case with all gases, its solubility diminishes as the temperature of the solution rises.

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* Or a mixture of potassium nitrate and ammonium sulphate, which gives ammonium nitrate and potassium sulphate by double decomposition.

The gas has a sweetish smell, and if inhaled in small quantities it causes a sensation of hilarity (for which reason it is sometimes called 'laughing gas'); in larger quantities it produces unconsciousness, and is used for this purpose in dentistry and in small surgical operations. The gas does not burn. A glowing chip placed in it bursts into flame;* carbon and phosphorus also burn in it brightly, and it is easily proved that carbon dioxide and phosphorus pentoxide respectively are produced. It is obvious, therefore, that the gas contains either free or combined oxygen.

Now *free* oxygen in a gaseous mixture can be detected with the aid of nitric oxide (p. 244). If some nitric oxide is bubbled into some of the (air-free) gas obtained from ammonium nitrate and confined over mercury or water, the red gas nitrogen tetroxide (p. 246) is not formed. The gas, therefore, is a *compound* of oxygen, and as it is formed from ammonium nitrate, $(NH_4)NO_3$, it may also contain combined nitrogen or hydrogen or both.

When the gas, dried with calcium chloride, is passed over strongly heated iron, an oxide of the metal is formed and nitrogen is liberated (compare nitric oxide, p. 244); water is not produced, as is the case with nitric acid (p. 238). Hence the gas is a compound of nitrogen and oxygen, and is called **nitrous oxide.** Now the *density* of the gas is 22, and therefore its molecular weight is 44; its molecular formula is thus found to be N_2O, since $2 \times 14 + 16 = 44$.

This conclusion may be confirmed by exploding nitrous oxide with hydrogen, when it is found that a mixture of 1 volume of nitrous oxide and 1 volume of hydrogen gives water (which condenses) and 1 volume of nitrogen. This result is expressed by the equation,

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* As a large proportion of water vapour is formed, as well as the gas, on heating ammonium nitrate, and as the gas collected over hot water contains so much aqueous vapour that it generally extinguishes a glowing chip, the samples used in these experiments may be dried with the aid of quicklime (compare fig. 75, p. 262) and collected by the upward displacement of air (p. 261).

$$N_2O + H_2 = N_2 + H_2O$$
$$1 \text{ vol.} + 1 \text{ vol.} = 1 \text{ vol.},$$

and could only be obtained with a compound of the molecular formula N_2O. The formation of nitrous oxide from ammonium nitrate is represented thus,

$$(NH_4)NO_3 = N_2O + 2H_2O.$$

The different compounds of nitrogen and oxygen which have now been described (pp. 240, 243, 246, 268) afford an excellent illustration of the law of multiple proportions. The analysis of these compounds shows that they have the following percentage compositions:

	Nitrous Oxide.	Nitric Oxide.	Nitrogen Tetroxide.	Nitrogen Pentoxide.*
Nitrogen . .	63·7	46·7	30·5	26·0
Oxygen . .	36·3	53·3	69·5	74·0

If now the weights of oxygen combined with a fixed weight of nitrogen, say with 1 g., are calculated, the following values are obtained,

	Nitrous Oxide.	Nitric Oxide.	Nitrogen Tetroxide.	Nitrogen Pentoxide.
Nitrogen . .	1	1	1	1
Oxygen . .	0·57	1·14	2·28	2·85

that is to say, the weights of oxygen which combine with a fixed weight of nitrogen are in the simple ratio, 1 : 2 : 4 : 5; and these facts are expressed by the formulæ, N_2O, NO, N_2O_4, and N_2O_5.†

The difference between a *compound* of nitrogen and oxygen and a *mixture* of nitrogen and oxygen, such as the air, is also emphasised by these data. In the former the elements are present in simple ratios of their atomic weights, which is the case with all compounds, since they are formed by the combination of indivisible atoms in fixed proportions; in the case of air and other mixtures of elements there is no necessary relation between the relative weights of their components, which may be present in any proportion.

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* Another oxide of nitrogen, N_2O_3, is known.

† This is also clearly seen by considering the number of oxygen atoms which would be present in any weight of gas which contained 28 units or *two* atoms of nitrogen; the numbers would be 1, 2, 4, and 5 respectively.

CHAPTER XXX.

Acids Composed of Carbon, Hydrogen, and Oxygen.

Carbonic Acid and its Salts.

An aqueous solution of carbon dioxide has a sharp taste and turns blue litmus a dull-red colour; it chemically dissolves certain metals (magnesium, iron), giving hydrogen and a salt of the metal, and also neutralises basic hydroxides, such as calcium hydroxide and sodium hydroxide, forming salts ($CaCO_3$, Na_2CO_3). The examination of these salts shows that they are derived from an acid of the formula H_2CO_3, and it is therefore concluded that the aqueous solution of carbon dioxide contains a compound, H_2CO_3, which is called **carbonic acid**, and which is formed by the combination of carbon dioxide and water, just as sulphurous acid, H_2SO_3, is formed from sulphur dioxide and water (p. 235); carbon dioxide, therefore, is also called **carbonic anhydride** (p. 233).

Carbonic acid, like sulphurous acid, only exists in aqueous solution; when its solution is evaporated, the acid is decomposed and carbonic anhydride escapes. Carbonic acid is dibasic (p. 254); many of its salts, which are called **carbonates**, are of great importance.

Normal calcium carbonate has already been described (p. 70); its formation from calcium hydroxide and carbonic acid is expressed by the equation,

$$Ca(OH)_2 + H_2CO_3 = CaCO_3 + 2H_2O.$$

When it is strongly heated it decomposes ($CaCO_3 = CaO + CO_2$), and when placed in hydrochloric, sulphuric, or nitric acid, it gives carbon dioxide, water, and a salt of the acid which is used,

$$CaCO_3 + 2HCl = CO_2 + H_2O + CaCl_2$$
$$CaCO_3 + H_2SO_4 = CO_2 + H_2O + CaSO_4.$$

When a little calcium carbonate is suspended in water, and carbon dioxide is bubbled through the suspension, the calcium carbonate slowly disappears; the normal salt and the acid act on one another, forming **calcium hydrogen carbonate** (a hydrogen salt), just as normal sodium sulphate and sulphuric acid give sodium hydrogen sulphate (p. 258),

$$CaCO_3 + H_2CO_3 = Ca(HCO_3)_2$$
$$Na_2SO_4 + H_2SO_4 = Na_2(HSO_4)_2 \text{ or } 2NaHSO_4.$$

Calcium hydrogen carbonate (often called calcium bicarbonate) is soluble in water, so that when a stream of carbon dioxide is passed through lime-water, although *insoluble* calcium carbonate is precipitated at first, the precipitate disappears again, as just stated, when the stream of gas is continued, owing to the formation of the *soluble* calcium hydrogen carbonate. When a solution of this salt is boiled, the salt decomposes, carbon dioxide is evolved, and calcium carbonate is precipitated,

$$Ca(HCO_3)_2 = CO_2 + H_2O + CaCO_3.$$

When lime-water is added to a solution of calcium hydrogen carbonate, the normal salt is formed (and precipitated), just as normal sodium sulphate is produced on adding sodium hydroxide to sodium hydrogen sulphate,

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$$
$$NaHSO_4 + NaOH = Na_2SO_4 + H_2O.$$

Magnesium carbonate, $MgCO_3$, is very similar to calcium carbonate in most respects, and occurs in nature as *magnesite;* it is also contained in dolomite or magnesian limestone, a rock very similar to limestone, but which is a mixture of calcium and magnesium carbonates, often coloured by small quantities of iron compounds (p. 75).

Magnesium hydrogen carbonate, $Mg(HCO_3)_2$, is formed from the normal salt, $MgCO_3 + H_2CO_3 = Mg(HCO_3)_2$, and is very similar to calcium hydrogen carbonate in properties.

Dilute aqueous solutions of calcium hydrogen carbonate and of magnesium hydrogen carbonate occur in nature. When rain and other natural waters which contain dissolved carbon dioxide (carbonic acid) come into contact with limestone, marble, chalk (or dolomite), calcium (or magnesium) hydrogen carbonate is formed and passes into solution. Sometimes the solution then runs to the roof of a cave or fissure in the rock, remains suspended for some time, and then drops; during its exposure to the air the solution evaporates, some of the soluble hydrogen carbonate is converted into the insoluble carbonate (carbon dioxide escaping), and this salt is deposited as an extremely thin layer on the roof and floor of the cave. During countless ages a sort of icicle of calcium carbonate is formed above, and a conical hill or pedestal rises to meet it below; these formations, often translucent and beautifully coloured, are known as *stalactites* and *stalagmites* respectively.

The presence of the hydrogen carbonates of calcium and magnesium in natural waters greatly affects the behaviour of such waters when they are used for domestic and manufacturing purposes; thus when such waters are boiled, they give a precipitate of the normal carbonate, part of which may adhere to the vessel, forming a stony layer or deposit ('fur' of kettles, boiler incrustations) which is a very bad conductor of heat, and which may choke up connecting-pipes. Further details are given later (p. 280).

Sodium carbonate, Na_2CO_3, has already been described; it separates from water in hydrated efflorescent crystals (soda-crystals), $Na_2CO_3, 10H_2O$, and although it is a *normal* salt, its solution has an alkaline reaction to litmus. The anhydrous salt melts at a bright-red heat, but does not decompose.

A solution of sodium carbonate is used in the preparation of other carbonates; thus with solutions of (*a*) copper nitrate, (*b*) calcium sulphate, and (*c*) calcium hydroxide, sodium carbonate gives a precipitate of copper carbonate or calcium carbonate as the case may be,

(*a*) $Cu(NO_3)_2 + Na_2CO_3 = CuCO_3 + 2NaNO_3$ (p. 45)
(*b*) $CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$
(*c*) $Ca(OH)_2 + Na_2CO_3 = CaCO_3 + 2NaOH$ (p. 78).

In these double decompositions an *insoluble* carbonate is formed and precipitated (compare p. 149).

Sodium carbonate is manufactured in large quantities from sodium chloride (common salt). In the Le Blanc process, which was worked out by a French apothecary of that name, sodium chloride is first converted into sodium sulphate (*salt-cake*) by heating it with sulphuric acid,

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl,$$

and the hydrogen chloride which is evolved is dissolved in water, the solution forming *commercial hydrochloric acid.*

The sodium sulphate is then heated with coal-dust and crushed limestone in suitable furnaces, the final result of which is the formation of sodium carbonate, calcium sulphide, and carbon dioxide,

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$
$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The black product (*black-ash*) is treated with water, which dissolves the sodium carbonate, leaving a residue (*alkali-waste*) of highly impure calcium sulphide; the *hot* aqueous solution, after having been evaporated, gives crystals, Na_2CO_3, H_2O, which are then heated to expel the water of crystallisation, the dehydrated salt being sold as soda-ash or calcined soda. If the crystals are deposited at *ordinary temperature* soda-crystals are obtained.* These and other commercial products are often very impure owing to the reactions being incomplete, or to secondary reactions taking place, or to contamination with iron and other materials used in the construction of the apparatus; thus commercial soda-ash obtained by this process usually contains only about 85 per cent. of Na_2CO_3.

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* Many substances behave like Na_2CO_3 and take up different proportions of water of crystallisation at different temperatures, but under fixed conditions the relative weights of the substance and of the water are constant.

In the Solvay, or ammonia-soda, process for the manufacture of sodium carbonate, carbon dioxide is passed into a solution of sodium chloride containing ammonium hydroxide; sodium hydrogen carbonate, which is relatively sparingly soluble in the *solution*, is precipitated,

$$NaCl + CO_2 + NH_4(OH) = NaHCO_3 + NH_4Cl,$$
$$\text{or} \quad CO_2 + NH_4OH = NH_4HCO_3,$$
$$\text{and} \quad NH_4HCO_3 + NaCl = NaHCO_3 + NH_4Cl.$$

This salt (see below) is separated and is gently heated, whereupon it is converted into normal carbonate, water, and carbon dioxide; the product is almost pure,

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

Sodium carbonate is used in the manufacture of soap and glass, in the bleaching and dyeing industries, and in the manufacture of caustic soda (sodium hydroxide, p. 78). For the purpose last mentioned, the solution obtained by treating 'black-ash' with water (p. 274) is heated with the right proportion of milk of lime; calcium carbonate is formed, and after being allowed to settle, the clear caustic liquor is run off and then evaporated in iron pans.

Sodium hydrogen carbonate, $NaHCO_3$, may be prepared by passing carbon dioxide through chambers containing soda-crystals placed on gratings; the gas is slowly absorbed, giving the anhydrous hydrogen salt, water escaping,

$$Na_2CO_3, 10H_2O + CO_2 = 2NaHCO_3 + 9H_2O.$$

The solubility of this salt at 15° is about 9; its solution has a neutral reaction to litmus although it is a hydrogen salt; the salt decomposes when its aqueous solution is boiled or when it is heated alone, the normal salt being formed (see above).

Sodium hydrogen carbonate mixed with some harmless vegetable acid such as tartaric acid (p. 282) is used in baking; the carbon dioxide which is liberated when the mixture (baking powder) is damped or heated makes the dough porous. Similar mixtures, sweetened and flavoured, are used in making effervescing drinks.

Potassium carbonate, K_2CO_3, is a salt very similar to sodium carbonate in most respects. Potassium compounds occur in all plants, and the ash which remains when vegetable matter is burnt is rich in potassium carbonate. At one time potassium carbonate was obtained almost entirely from wood ashes; the ashes were treated with water and the solution boiled down in pots, the residue being known as '*potashes*.' Crude potashes are very impure; the purified material is known commercially as *pearl-ash*, and is used in making soft soap and caustic potash, KOH. Potassium carbonate is very soluble in water (its solubility is 112 at 20°), and although it is a normal salt, its aqueous solution is alkaline to litmus.

Ammonium hydrogen carbonate, $(NH_4)HCO_3$, is formed when excess of carbon dioxide is passed into a solution of ammonium hydroxide, and is obtained in crystals when the solution is evaporated; it volatilises when it is heated. The '**ammonium carbonate**' of commerce is obtained by heating a mixture of ammonium chloride and calcium carbonate; the product, which sublimes, leaving a residue of calcium chloride, is a mixture of ammonium hydrogen carbonate and another ammonium salt (ammonium carbamate).

The *normal* carbonates of most of the common metals are insoluble in water, and are decomposed at relatively low temperatures (compare copper carbonate, p. 45), giving carbon dioxide and an oxide of the metal. All carbonates are decomposed by acids just as is calcium carbonate, so that they are often used in making other salts.

ACETIC ACID.

The liquid which is collected when wood is submitted to destructive distillation (p. 114) in iron retorts separates into two layers. The lower one is a black, 'tarry' mixture of many compounds, and is called wood creosote; it is used for preserving wood, as it prevents the growth of moulds, &c. The upper layer, a dark-brown, watery solution called pyroligneous acid, contains two important compounds, namely, *acetic acid* and methyl alcohol or wood-spirit (p. 127). When this aqueous solution is neutralised with milk of lime the acetic acid is converted into a salt, *calcium acetate*, which is not volatile; on the liquid being then heated, the volatile methyl alcohol and water pass off and are condensed, a brown solid residue of calcium acetate remaining in the retort.

When calcium acetate is mixed with sulphuric acid, acetic acid and calcium sulphate are formed, and the former, being volatile, can be separated from the latter by distillation. After other operations the crude acetic acid is cooled, and the crystals of the acid which are then formed are separated from the mother liquor, which contains water and other impurities.

Acetic acid forms colourless crystals which melt at 16·7°; as it is hygroscopic and its melting-point is lowered by the presence of water (compare p. 10), it is seldom seen as a solid except in winter.* It is miscible with water, and its aqueous solution has a sour taste, turns blue litmus red, and chemically dissolves some metals, forming salts, hydrogen being liberated.

The vapour of acetic acid burns with a non-luminous flame, water and carbon dioxide being formed.

The percentage composition of acetic acid may be found by burning a known weight of the pure compound exactly as described in the case of sugar, and weighing the products of combustion; the results show that acetic acid contains 40·0 per cent. of carbon, 6·66 per cent. of hydrogen, and (by difference, p. 125) 53·3 per cent. of oxygen. Dividing these numbers by the atomic weights of the respective elements and then simplifying the ratio, the *empirical* formula (p. 202) of acetic acid is found to be CH_2O,

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* Acetic acid which contains only a little water, and which therefore freezes easily to an ice-like mass, is called *glacial* acetic acid.

$$\left.\begin{array}{lr} \text{Carbon,} & 40{\cdot}00 \div 12 = 3{\cdot}33 \\ \text{Hydrogen,} & 6{\cdot}66 \div 1 = 6{\cdot}66 \\ \text{Oxygen,} & 53{\cdot}33 \div 16 = 3{\cdot}33 \end{array}\right\} \text{and } 3{\cdot}33 : 6{\cdot}66 : 3{\cdot}33 \text{ as } 1:2:1.$$

Now the density of acetic acid vapour is found to be about 30; therefore the molecular weight of the compound is 60, and its molecular formula is $C_2H_4O_2$ $(24+4+32)$.

When acetic acid is treated with sodium carbonate, carbon dioxide is evolved, and *sodium acetate* is formed; after the solution has been concentrated, this salt separates in colourless hydrated crystals, which are readily soluble in water. Concentrated aqueous solutions of sodium acetate and silver nitrate mixed together give a colourless crystalline precipitate of **silver acetate**; this salt is only sparingly soluble in cold water, with which it may be 'washed.'

Silver acetate is decomposed when it is heated, giving gaseous products and a residue of silver; by heating a known weight of pure (dry) silver acetate and weighing the residue the percentage of silver may be determined.

A complete analysis of silver acetate may be made in the same way as that of acetic acid, the residue of silver being also weighed; from the percentage results, which are given below (oxygen, by difference), the formula of silver acetate is found to be $C_2H_3AgO_2$ or $AgC_2H_3O_2$,

$$\begin{array}{lrl} C & = 14{\cdot}4 \div 12 = 1{\cdot}2 & \text{and } 1{\cdot}2 \div 0{\cdot}6 = 2 \\ H & = 1{\cdot}8 \div 1 = 1{\cdot}8 & \text{and } 1{\cdot}8 \div 0{\cdot}6 = 3 \\ Ag & = 64{\cdot}4 \div 107 = 0{\cdot}6 & \text{and } 0{\cdot}6 \div 0{\cdot}6 = 1 \\ O & = 19{\cdot}3 \div 16 = 1{\cdot}2 & \text{and } 1{\cdot}2 \div 0{\cdot}6 = 2. \end{array}$$

This and many other facts show that although acetic acid contains four atoms of hydrogen, only one of these atoms is displaced when the acid forms salts; acetic acid, therefore, is *monobasic* (p. 254).

The metallic salts of acetic acid, the *acetates*, are all soluble in water. **Sodium acetate**, $NaC_2H_3O_2 + 3H_2O$, and **calcium acetate**, $Ca(C_2H_3O_2)_2 + H_2O$, may be prepared in the laboratory by neutralising the acid with the corresponding basic hydroxide,

$$2C_2H_4O_2 + Ca(OH)_2 = Ca(C_2H_3O_2)_2 + 2H_2O,$$

or by treating the acid with the corresponding carbonate,

$$2C_2H_4O_2 + Na_2CO_3 = 2NaC_2H_3O_2 + CO_2 + H_2O.$$

Lead acetate, $Pb(C_2H_3O_2)_2 + 3H_2O$, is prepared by chemically dissolving oxide of lead in acetic acid,

$$PbO + 2C_2H_4O_2 = Pb(C_2H_3O_2)_2 + H_2O,$$

and evaporating the solution; it has a sweetish taste, and is commonly known as 'sugar of lead,' but, like all soluble lead salts, it is very poisonous.

Vinegar is water containing 4–10 per cent. of acetic acid and small quantities of various other compounds which give it colour and aroma; it is prepared from weak wines and other liquids which contain alcohol (p. 126).

FATTY ACIDS AND SOAPS.

Vegetable oils, such as palm oil and cocoa-nut oil, and animal fat (lard, suet-fat) are insoluble in water, but when such oils and fats are boiled with caustic soda solution, the compounds contained in them are decomposed, and a 'soapy' aqueous solution results. On adding salt (sodium chloride) to this aqueous solution, there is formed a curdy precipitate, which can be separated and pressed.* This product is ordinary hard soap (which may be scented and coloured before it is sold).

When an acid is added to an aqueous solution of soap, a pasty or fatty mass separates, and it has been found that this material is a mixture of several acids, all of which, like acetic acid, are compounds of carbon, hydrogen, and oxygen. The principal acids which are thus obtained from soap (and therefore from vegetable oils and fats) are **palmitic** and **stearic acids** (two compounds which are very like fat in outward properties, and which are called *fatty acids*) and an oily liquid called **oleïc acid.** A mixture of these two fatty acids with a little paraffin wax is used for the manufacture of stearin candles, commonly called wax candles.

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* Soap is soluble in pure water, but not in very salt water.

Ordinary hard soap consists principally of a damp mixture of the *sodium* salts of palmitic, stearic, and oleïc acids. Soft soap is a mixture of the *potassium* salts of these acids, and is prepared by heating oils and fats with potassium carbonate (p. 276) instead of with caustic soda or sodium carbonate.

Hard and Soft Waters.

When shavings of soap are vigorously shaken with distilled water for about a minute, an opalescent solution is obtained, and a great froth or lather, which remains for some minutes after shaking has ceased. If now any aqueous solution of a calcium or magnesium salt is added, and the solution is again shaken, the lather breaks down, and an insoluble curdy scum is formed. The reason is that the soluble sodium salts of the palmitic, stearic, and oleïc acids and the soluble calcium or magnesium salt act on one another, giving *insoluble* calcium or magnesium salts of the three acids just named. This double decomposition may be exemplified thus,

$$\begin{array}{c}\text{Sodium}\\\text{stearate}\end{array} + \begin{array}{c}\text{calcium}\\\text{sulphate}\end{array} = \begin{array}{c}\text{calcium}\\\text{stearate}\end{array} + \begin{array}{c}\text{sodium}\\\text{sulphate.}\end{array}$$

Now with some kinds of natural waters soap behaves as it does with distilled water, and gives a solution and a good permanent lather, but no curd. Such waters are free from calcium and magnesium salts, and are called '*soft waters.*' Many natural waters, however, contain one or more of the following salts,

I. Calcium hydrogen carbonate, $Ca(HCO_3)_2$; magnesium hydrogen carbonate, $Mg(HCO_3)_2$;
II. Calcium sulphate, $CaSO_4$; magnesium sulphate, $MgSO_4$; calcium chloride, $CaCl_2$; magnesium chloride, $MgCl_2$;
and all such waters give with soap curdy masses instead of a lather. Such are called '*hard waters.*'

Hard waters, however, are different in behaviour according as they contain salts of group I. or group II. The salts of group I. are decomposed when the water is boiled, and are precipitated as insoluble normal carbonates (p. 271),

$$Ca(HCO_3)_2 = CaCO_3 + CO_2 + H_2O,$$

so that when the boiled water is run off from the deposit it is then quite soft, and gives a clear solution and a permanent lather with soap. Waters containing the salts of group I. have thus come to be called 'temporarily hard' waters, and their hardness is spoken of as 'temporary hardness.' Such temporarily hard waters may also be softened by adding to them a quantity of milk of lime equivalent to (p. 176) the calcium hydrogen salt present. This salt *and* the calcium hydroxide are thus converted into and precipitated as insoluble normal carbonate, and the water is then free from soluble calcium salts,

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$

Similarly with magnesium hydrogen carbonate,

$$Mg(HCO_3)_2 + Ca(OH)_2 = MgCO_3 + CaCO_3 + 2H_2O.$$

This process for softening temporarily hard waters is known as Clarke's process. Unless such temporarily hard waters are softened, they give rise to dense boiler incrustations when they are used for raising steam, and thus cause a great waste of fuel and the risk of boiler explosions. Waters containing salts of group II. are not softened when they are boiled, as these salts are not converted into insoluble precipitates. Such waters are called 'permanently hard' waters.

When a solution of sodium carbonate is added to a permanently hard water, the sulphates and chlorides of calcium and magnesium are precipitated as insoluble carbonates,

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$
$$MgCl_2 + Na_2CO_3 = MgCO_3 + 2NaCl,$$

and, as the soluble sodium salts formed at the same time do not act on soap, the clear water is soft. This is why 'washing soda' is used for laundry-work, and for softening permanently hard waters for other purposes. When sodium carbonate is not used, the soap must be added until all the soluble calcium and magnesium salts have been converted into insoluble stearates (&c.); this leads to a waste of soap, and the presence of the insoluble curd has also many disadvantages.

The hardness of a natural water is generally due to the presence of salts of *both* the groups I. and II.; that is to say, the 'hardness' is partly temporary, partly permanent. Such waters, however, may be softened by combining the two processes described above, and in other and better ways.

The 'hardness' of a water may be measured by finding how much soap solution of a certain *standard* strength is required to produce a permanent lather when it is shaken with a given volume of the hard water. The 'hardness' is then stated in certain units which are called 'degrees of hardness.'

Tartaric acid.—Wine which has been kept for some time often contains a coloured crystalline deposit (*argol*), which is sparingly soluble in cold water and consists principally of potassium hydrogen tartrate. Tartaric acid is prepared from this salt.

Tartaric acid forms colourless crystals, and melts at 167°. It decomposes when heated more strongly, giving a charred (carbonaceous) mass, which burns away completely when it is heated in the air. The acid is readily soluble in water. Its solution has a sour taste, turns blue litmus red, and decomposes carbonates, liberating carbon dioxide and forming *tartrates*.

Tartaric acid has the formula $C_4H_6O_6$, and is *dibasic.* Its normal *potassium salt*, $K_2C_4H_4O_6$, is readily soluble in water, but its *potassium hydrogen salt*, $KC_4H_5O_6$, is only sparingly soluble.

Citric acid, another 'vegetable acid,' occurs in and is obtained from lemon juice. It is a colourless, crystalline *tribasic* acid, and has the formula $C_6H_8O_7$.

Oxalic acid, $C_2H_2O_4 + 2H_2O$, occurs in certain plants (rhubarb, sorrel), and can be prepared from sawdust. Its crystals are hydrated and readily soluble in water, the solution showing the ordinary properties of an acid; the acid is dibasic, and is very poisonous.

When oxalic acid is gently heated with sulphuric acid it is decomposed, giving carbon monoxide (p. 120), carbon dioxide, and water,*

$$C_2H_2O_4 = CO + CO_2 + H_2O.$$

The carbon dioxide may be absorbed by passing the mixed gases through wash-bottles containing sodium hydroxide solution, and the carbon monoxide, when dried, is obtained in a state of purity.

CHAPTER XXXI.

Oxidation and Reduction.

Many naturally occurring compounds or mixtures (sugar, starch, coal, wood, &c.) undergo 'combustion' in air or in oxygen; in all these cases the products of combustion are *oxides.* Most of the elements also combine with oxygen, often with development of light and heat, giving the corresponding *oxides.* The frequent occurrence of such changes and their general importance led to the use of the term *oxidation* to express any change leading to the formation of an oxide.

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* The sulphuric acid is not decomposed, and therefore does not appear in the equation.

Thus the rusting of iron, the burning of coal-gas or of 'petrol,' the 'decay' of vegetable matter, the conversion of food in the body into carbon dioxide and other products, are processes of oxidation; the materials are said to be *oxidised*, and the products are called *oxidation products.*

Many metallic oxides may be brought back or reduced to the metal by heating them with coal, charcoal, or other materials containing carbon. The term *reduction* was applied to processes of this kind in which oxygen was removed (in a combined form) from an oxide. Thus the conversion of copper oxide into copper (and water) with the aid of hydrogen is a process of reduction; the copper oxide is said to be *reduced*, and the metal is the *reduction product.*

Now some elements form two (or more) compounds with oxygen, in which case the one containing the smaller proportion of oxygen is called the *lower* oxide, the other the *higher* oxide. Obviously the conversion of a lower into a higher oxide is a process of oxidation, and the reverse change a process of reduction. Thus carbon monoxide undergoes oxidation to carbon dioxide when it burns; carbon dioxide is reduced to carbon monoxide when it is heated with carbon. Sulphur dioxide may be oxidised to sulphur trioxide; lead dioxide may be reduced to lead monoxide (p. 178).

In the course of time the use of the term oxidation has been extended to processes in which oxygen is not directly concerned; the reason of this is as follows. A basic metallic oxide and an acid act on one another, forming a salt and water; the acid radicle takes the place of the oxygen of the metallic oxide, and the salt thus formed *corresponds with* or is derived from the oxide,

$$\mathrm{PbO + 2HCl = PbCl_2 + H_2O}$$
$$\mathrm{CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O.}$$

Hence the conversion of a metal into a salt either (*a*) by first forming the oxide and then acting with an acid, or (*b*) by treating the metal directly with an acid, is a process of 'oxidation;' in fact, the combination of a metal with any element except hydrogen or other metals is a change which may be included under this heading. Thus the combination of iron with sulphur ($Fe + S = FeS$) and of copper with chlorine ($Cu + Cl_2 = CuCl_2$) are oxidations, the non-metallic elements being regarded as playing a part similar to that of oxygen.

The removal of such acid radicles or non-metallic elements from a compound of a metal is consequently to be regarded as a process of reduction; thus when silver chloride is heated in hydrogen it is reduced to silver. Any element or compound which oxidises another element or compound is termed an *oxidising agent;* similarly, any element or compound which reduces another element or compound is termed a *reducing agent.* The commonest oxidising agent is oxygen, and many examples of its use have already been given.

Chlorine is an oxidising agent. When *dry* chlorine oxidises it does so by combining directly with the element or compound which undergoes oxidation (see above) or by withdrawing hydrogen from a compound;* thus chlorine *oxidises* hydrogen sulphide ($Cl_2 + H_2S = 2HCl + S$), the chlorine itself being *reduced* to hydrogen chloride. Chlorine also oxidises cuprous chloride, $CuCl$ (which corresponds with the lower oxide Cu_2O, p. 177), to cupric chloride, $CuCl_2$ (which corresponds with the higher oxide CuO).

Wet chlorine—that is to say, *chlorine* and *water*—acts as an oxidising agent in a different manner; the chlorine slowly decomposes the water, forming hydrogen chloride and a compound called *hypochlorous acid,*

$$Cl_2 + H_2O = HCl + HClO,$$

and the latter then acts as an oxidising agent, giving up oxygen and forming hydrogen chloride. The bleaching action of chlorine in presence of water (dry chlorine does not bleach) is thus due to the *oxidation* of the coloured compounds and their conversion into colourless ones by combination with *oxygen* and not with chlorine.

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* For various reasons which need not be given here, hydrogen is considered to be a metal, or so like the metals that it may be classed with them. The removal of hydrogen from a compound is thus considered to be a process of oxidation, whereas the combination of hydrogen with an element or compound is a reduction.

Bleaching powder, prepared by absorbing chlorine in dry slaked lime, contains a compound of calcium, oxygen, and chlorine, which is a powerful oxidising agent. In bleaching on the large scale, the fabric is passed through or immersed in a solution of bleaching powder, and is then washed with water; or, before washing with water, it is exposed to the air or passed through chambers containing carbonic acid, which liberates hypochlorous acid from the bleaching powder.

Manganese dioxide, MnO_2, acts as an oxidising agent when it is warmed with hydrochloric acid, as in the preparation of chlorine (p. 140),

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O\,;$$

the salt *manganese chloride*, $MnCl_2$, which is formed in this reaction corresponds with or is derived from the lower oxide, *manganous oxide*, MnO, since

$$MnO + 2HCl = MnCl_2 + H_2O.$$

Nitric acid is another important oxidising agent, as it readily acts on many substances, giving them oxygen, and being itself reduced to *nitrous acid*, HNO_2 (p. 247), or to one of the oxides of nitrogen (compare its action on copper, p. 245, and tin, p. 246). Thus when hydrogen sulphide is passed into excess of nitric acid, sulphur is deposited, the hydrogen sulphide being first oxidised to sulphur;* on heating, the sulphur is oxidised to sulphur trioxide and sulphuric acid is formed. When sulphur dioxide is passed into nitric acid it is rapidly oxidised to sulphur trioxide (which in presence of water gives sulphuric acid), and nitrous acid is formed by reduction,

$$SO_2 + H_2O + HNO_3 = H_2SO_4 + HNO_2.$$

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* See footnote, preceding page.

This oxidising action of nitric acid is made use of commercially in the manufacture of sulphuric acid by the '*leaden chamber process.*' Into chambers constructed of sheet-lead (a metal which is very slowly attacked by sulphuric acid) *steam*, *air*, and *sulphur dioxide* are passed in constant streams, also a little *nitric acid* vapour. The sulphur dioxide is generally obtained by burning (or roasting) iron pyrites, FeS_2, in the air (p. 229); sulphur dioxide and ferric oxide, Fe_2O_3, are thus formed,

$$4FeS_2 + 11O_2 = 8SO_2 + 2Fe_2O_3.$$

Now although sulphur dioxide and sulphurous acid do not combine with free oxygen except extremely slowly (p. 231), they do so rapidly when they are mixed with it in presence of a relatively very small quantity of nitric acid. The first action of the nitric acid is to oxidise the sulphur dioxide to the trioxide (or the sulphurous to sulphuric acid); in this process the nitric acid is reduced first to nitrous acid (p. 286), and then to nitric oxide (p. 243),

$$2HNO_2 + SO_2 = H_2SO_4 + 2NO.$$

Now nitric oxide combines with *atmospheric oxygen* to form nitrogen tetroxide (p. 246), and nitrogen tetroxide oxidises sulphur dioxide, being itself reduced to nitric oxide again,

$$2NO + O_2 = N_2O_4$$
$$N_2O_4 + 2SO_2 = 2NO + 2SO_3;$$

hence there is a continuous oxidation of the sulphur dioxide to sulphur trioxide (which in presence of water forms sulphuric acid), and the oxygen which is fixed in this process is *atmospheric* oxygen. The nitric oxide which really brings about this change is not used up, and provided it is not allowed to leave the chamber with the atmospheric nitrogen, a small quantity of this gas may serve for the preparation of an unlimited quantity of sulphuric acid. In practice there is some loss, so that small quantities of fresh nitric acid vapour must be supplied from time to time.

The gas nitric oxide here plays a part similar to that of the catalytic agent platinum, which is used in making sulphuric acid by the contact process (p. 232); it accelerates the combination of sulphur dioxide and oxygen, and is itself unchanged at the *end* of the process. There is, however, a difference between the two cases. With the platinum, there is no evidence that the metal *combines* with the oxygen and then gives it up again to the sulphur dioxide; it may do so, and probably does; but if so, the fact has not been established. It is quite possible that in all cases of catalysis the catalytic agent is chemically changed, forming a substance, very unstable under the given conditions, which decomposes or acts on another substance present, giving the observed product.

The most important reducing agents at high temperatures are carbon, carbon monoxide, and hydrogen. When the oxides of iron, lead, copper, tin, or zinc are *heated* with one of these reducing agents, the metal is obtained and an oxide of carbon, or water, as the case may be, is formed.* On the large scale these metals are prepared from their oxides by heating the latter with coke, charcoal, or coal. In these processes the carbon of the fuel may act directly and undergo oxidation to carbon monoxide, or it may be first burnt to carbon monoxide by admitting a limited supply of atmospheric oxygen (p. 132), in which case the carbon monoxide thus formed is the active reducing agent. Thus in preparing zinc the change takes place in absence of air, and may be expressed thus,

$$ZnO + C = Zn + CO;$$

whereas in the case of iron a blast of air is sent through the furnace, and it is the carbon monoxide produced from the fuel which then reduces the oxide of iron,

$$C + O_2 = CO_2; \quad CO_2 + C = 2CO$$
$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

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* A very high temperature is required to bring about some of these changes.

Hydrocarbons (p. 125), and, in fact, nearly all carbon compounds, are also reducing agents at high temperatures, since they combine with oxygen, giving carbon dioxide and water.

A study of the examples given above shows that nearly all the reactions which have been taken to illustrate *oxidation* might equally well be chosen to illustrate *reduction*, and *vice versâ*. When an oxidising agent oxidises, it is itself reduced. Chlorine is reduced to hydrogen chloride by hydrogen sulphide; nitric acid is reduced first to nitrous acid and then to nitric oxide by sulphur dioxide; hence hydrogen sulphide and sulphur dioxide are reducing agents.

When a reducing agent reduces, it is itself oxidised. Carbon, carbon monoxide, and hydrogen are oxidised by certain metallic oxides at high temperatures. Some substances act as oxidising *or* as reducing agents according to the element or compound on which they act; thus sulphur dioxide reduces nitric acid, but in presence of water, it oxidises hydrogen sulphide to sulphur and water,

$$SO_2 + 2H_2S = 2H_2O + 3S,$$

and is itself reduced to sulphur.

When sulphur dioxide (in presence of water) and sulphurous acid are used as bleaching agents, they either reduce the coloured substance by supplying hydrogen, or they combine with it; if the former, the hydrogen is obtained from the water present by the *combined* action of the sulphurous acid and the coloured substance, while the acid is oxidised to sulphuric acid.

CHAPTER XXXII.

The Principal Components of the Earth's Crust.

The bare rocks which are exposed to view in different parts of this and other countries are often very different from one another in appearance and in other properties. They may consist of granite, as at Land's End; of chalk, as at Dover; of sandstone, as in many parts of Devonshire; of slate, as in many parts of Wales; and so on. These and very many other varieties of 'rock' are classed into two groups: (*a*) the *igneous* and (*b*) the *sedimentary* rocks.

The *igneous* rocks, such as granite, basalt, porphyry, &c., were at one time in a molten state, and slowly solidified during the cooling of the earth's crust, or have been thrown up in more recent times by volcanic action. They are composed principally of oxides of the elements silicon, aluminium, calcium, magnesium, iron, sodium, and potassium, and these oxides are either mixed or combined with one another in various proportions, the products of their combination being *salts.* Thus in a sample of *granite,* so called because of its *grained* structure, distinct crystals of *felspar*, *quartz*, and *mica* may generally be recognised; the crystals may be silvery-white or transparent, or may be coloured red or yellow, or darkened, by the presence of small quantities of compounds of iron and other metals.

Felspar, of which there are many varieties, is composed of the oxides of silicon, aluminium, and potassium *or* sodium (*or* calcium). The oxide of silicon, known as silica (p. 292), is an acid-forming oxide, and it combines with the basic oxide of aluminium (alumina), forming the salt *aluminium silicate.* Silica also combines with the basic oxides of calcium, magnesium, potassium, and sodium, forming *silicates* of the respective metals. Felspar consists principally of aluminium silicate mixed with potassium silicate (forming *orthoclase*) or with sodium silicate (forming *albite*).

Mica, like felspar, is a mixture of different compounds; it consists principally of aluminium silicate, but contains also potassium silicate and other substances.

Although granite and other igneous rocks are extremely hard and durable, they are very slowly acted on by air and by natural water (both of which contain carbonic acid), and in the course of ages this action results in the breaking up or *disintegration* of the rock material.* The silicates of potassium and sodium contained in the felspar or mica are dissolved. The aluminium silicate and the quartz are both insoluble in water, but the former may be carried away as a fine powder by running water and deposited again in beds, which form the material known as *clay*. When this aluminium silicate is fairly pure it is white, and is known as *kaolin* or *china-clay*; it is generally coloured with iron compounds, and such impure clay, when 'burnt' (strongly heated in a kiln), loses water and becomes very hard, and is used for making bricks, tiles, and other coarse earthenware. Pure kaolin or china-clay is utilised in the manufacture of porcelain and the more expensive varieties of 'china,' for which purpose it is heated with suitable proportions of felspar and quartz.

The coarser particles of quartz (*silica*), resulting from the disintegration of igneous rocks, may also be washed away by running water, and in the course of time, although so hard, they become smooth and rounded. Beds or deposits of this material form ordinary *sand*. Sand which has been long exposed to the action of water, such as some sea-sands, consists of almost pure silica, all the felspar, mica, and other compounds having been disintegrated and washed away. Ordinary sand, however, contains unchanged fragments of these rock components, and is often coloured red or yellow by iron compounds. Layers of impure sand, containing clay, &c., which have been submitted to great pressure give rise to *sandstone;* layers of clay which have been compressed give rise to *slates* and *shales,* the latter often containing vegetable matter of the nature of coal.

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* This process is known as 'weathering.'

The sedimentary rocks are those, such as sandstone, clay, slate, &c., which have been formed from igneous rocks in the manner indicated; those, such as limestone, marble, chalk, and coral (p. 74), which have been formed from animal remains; and those, such as coal and anthracite, which have been formed from vegetable matter.

Silicon dioxide or **silica,** SiO_2, is the most important component of the earth's crust, where it occurs not only in the free state, but also combined with aluminium oxide or with other basic oxides; igneous rocks contain 20–36 per cent. of silica (free and combined). Silica is often found in pure, transparent, colourless crystals (*quartz* or *rock-crystal*), but sometimes the crystals are opaque (milk quartz) or coloured by traces of other compounds (rose quartz, smoky quartz). It also occurs in the animal kingdom in siliceous sponges; in the vegetable kingdom it is found in the 'straw' of cereals, in the stem of the bamboo, and in the skeletons of the *diatomaceæ.*

Just as from the remains of some organisms beds of calcium carbonate have been formed, so from the remains of diatomaceæ, beds of very fine silica have been produced. Such deposits occur, for example, in Germany; and the material, known as *kieselguhr*, is used as an absorbent for nitro-glycerine (the mixture is *dynamite*) and for filtering and other purposes.

Flint is an amorphous variety of slightly impure silica.

When sand or any other sample of impure silica (or any compound of silica) is mixed with about four times its weight of anhydrous sodium carbonate, and the mixture is strongly heated in a platinum crucible with the blowpipe flame, the sodium carbonate melts and the silica slowly dissolves chemically in the melted mass, liberating carbon dioxide; when the product is then allowed to cool and afterwards boiled with water, *sodium silicate* dissolves, and any other metals (except potassium and aluminium) which were originally present in a combined form remain as insoluble carbonates or oxides. The acid-forming oxide, silica, decomposes sodium carbonate at high temperatures, giving the salt, sodium (meta) silicate,

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2.$$

When the filtered solution containing sodium (meta) silicate is mixed with excess of hydrochloric acid and boiled, a colourless gelatinous precipitate of **metasilicic acid** is formed,

$$Na_2SiO_3 + 2HCl = H_2SiO_3 + 2NaCl.$$

This acid is insoluble in water, but dissolves chemically in a solution of sodium hydroxide, forming the soluble sodium salt. It is a dibasic acid.

When the gelatinous precipitate of metasilicic acid is separated by filtration, washed well, and then heated, it is decomposed into water and pure *silica*, which is obtained as a white amorphous powder.

Silica is extremely hard, melts only at a very high temperature, and is insoluble in water and in the ordinary acids. It is used for the manufacture of tubes, basins, &c. for use in chemical laboratories, as it resists the action of chemicals better than does glass, and does not crack when it is suddenly heated or cooled. Although such an inert substance, it is proved to be an acid-forming oxide (or anhydride) by the fact that it forms sodium silicate. Silica also combines with other basic oxides, forming salts; but all such *silicates* are insoluble in water, except those of sodium and potassium.

Ordinary *glass* is manufactured by strongly heating sand (crude silica) with a suitable proportion of a mixture of sodium carbonate and calcium carbonate. These carbonates are decomposed, with liberation of carbon dioxide,

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2,$$

and a mixture of sodium and calcium silicates, containing excess of silica, is formed. If the sand employed contains certain impurities (such as iron compounds) the glass may be coloured (green), and if a coloured glass is required the desired result is attained by adding the oxide of some metal to the above mixture.

The temperature at which ordinary glass softens depends very much on the proportion of silica it contains; *soft* or more easily fusible soda-glass contains a smaller proportion of silica than the *hard* or less fusible varieties. *Flint glass* is made by heating silica with sodium carbonate and lead oxide; it has a greater refractive power for light than ordinary glass, and is more easily fusible.

The element **silicon**, Si, is obtained when finely divided silica and magnesium are heated together, a violent reaction taking place,

$$SiO_2 + 2Mg = Si + 2MgO.$$

When the product is treated with dilute hydrochloric acid the magnesium oxide is converted into soluble magnesium chloride, leaving (impure) silicon as a brown powder, which takes fire and burns when it is heated in the air, giving silica.

Aluminium oxide or **alumina**, Al_2O_3, occurs in nature in various forms, and is very abundant. The ruby and the sapphire are crystalline varieties of alumina, coloured by traces of other compounds; corundum, a material almost as hard as diamond, also consists principally of alumina; while emery is a mixture of alumina and oxide of iron.

Alumina occurs combined with silica, as aluminium silicate, in felspar, mica, kaolin, and in ordinary clay (pp. 290, 291). When clay is heated with sulphuric acid the aluminium silicate is decomposed, silica separates, and **aluminium sulphate**, $Al_2(SO_4)_3$, passes into solution; on the solution being evaporated, this salt is obtained in crystals.

When potassium sulphate is dissolved in a hot solution of aluminium sulphate in suitable proportions, and the solution is evaporated if necessary and allowed to cool, colourless octahedral crystals of **potash alum** are deposited. These crystals contain one molecule of aluminium sulphate and one molecule of potassium sulphate crystallised together with twenty-four molecules of water, and their composition is expressed by the formula, $Al_2(SO_4)_3$, K_2SO_4, $24H_2O$. Potash alum is an important commercial article, used in dyeing and for other purposes. **Soda alum,** $Al_2(SO_4)_3$, Na_2SO_4, $24H_2O$; **ammonia alum,** $Al_2(SO_4)_3$, $(NH_4)_2SO_4 + 24H_2O$; and other 'alums,' may be prepared in a similar manner, using sodium or ammonium sulphate in the place of potassium sulphate. All these alums are readily soluble in hot, but only sparingly soluble in cold, water, so that they are easily purified by recrystallisation; they all crystallise in octahedra.

A salt, such as one of the alums, which is a crystalline mixture of two salts is called a *double salt.* Many other double salts are known.

When ammonium hydroxide is added to a solution of aluminium sulphate or of any alum, a colourless, flocculent precipitate of **aluminium hydroxide** is formed, and ammonium sulphate remains in solution,

$$Al_2(SO_4)_3 + 6NH_4(OH) = 2Al(OH)_3 + 3(NH_4)_2SO_4.$$

This hydroxide is insoluble in water, but dissolves chemically in hydrochloric and in sulphuric acid, forming aluminium salts; it is, therefore, a *basic hydroxide.* But aluminium hydroxide also dissolves chemically in a solution of sodium hydroxide, giving a soluble salt, **sodium aluminate**; in this case, therefore, aluminium hydroxide behaves like an *acid hydroxide* or acid.

Aluminium hydroxide is decomposed when it is heated, giving water and aluminium oxide, an amorphous powder insoluble in most acids,

$$2Al(OH)_3 = Al_2O_3 + 3H_2O.$$

When this oxide is strongly heated with carbon (in an electric furnace, p. 299) the oxide is reduced and the metal **aluminium** is obtained,

$$Al_2O_3 + 3C = 2Al + 3CO.$$

The metal derives its name from 'alum,' which was known long before the metal was discovered.

CHAPTER XXXIII.

The Use of Electricity in bringing about Chemical Change.

When zinc is placed in dilute sulphuric acid, the metal dissolves chemically, hydrogen is evolved at the surface of the metal, and zinc sulphate passes into solution.* A development of heat also occurs, and the quantity of heat generated during the conversion of a fixed weight of the metal into its sulphate under fixed conditions is constant (p. 135).

Copper, silver, and platinum are not acted on by dilute sulphuric acid, but when a piece of zinc is placed in direct contact with a piece of copper, silver, or platinum, and the two different metals are then immersed in dilute sulphuric acid, a very interesting result is observed. The zinc dissolves chemically, forming zinc sulphate, and hydrogen is evolved, *but* this gas is only liberated at the surface of the copper, silver, or platinum, while the metal from which it rises remains chemically *unchanged*.† The same results are observed when the two different metals, instead of being placed in contact, are separated from one another in the acid, but are connected together by a wire (say of copper) which remains outside the liquid, as shown in fig. 76. Further, the wire which thus connects the two different metals acquires totally new properties; not only does its temperature rise,‡ but it has also the power of deflecting a magnetic needle brought near to it. A *current of electricity* is said to pass through the wire from one metal to the other, and also through the solution, and this electric current continues as long as the zinc is being transformed into its sulphate.

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* Pure zinc is only very slowly attacked by dilute sulphuric acid.

† Pure zinc is employed in this experiment; when the impure metal is used some hydrogen is also evolved from the surface of the zinc. Pure zinc is readily attacked by dilute sulphuric acid when it is in contact with a piece of platinum or copper, or when a little copper sulphate is added with the acid; in the latter case copper is deposited on the zinc (p. 175).

‡ The rise in temperature may be very small unless the plates of metal are large.

In the arrangement just described the chemical energy of the original system (p. 136) is not transformed directly into heat alone, but partly into heat and partly into electrical energy.

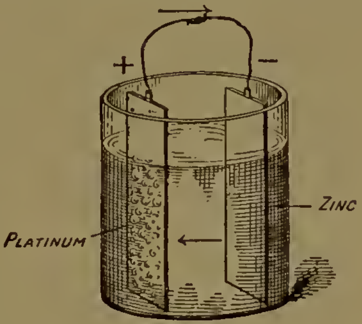

Fig. 76.

The apparatus (fig. 76) by means of which this transformation is brought about is called an *electric battery* (also a voltaic or galvanic battery, or cell, or couple). Any two different metals, placed in any liquid which chemically attacks at least one of them, and connected together outside the liquid by some *conductor*, may constitute a battery, provided that the liquid also is a conductor of electricity.

The term *conductor* is applied to those materials, such as metals, alloys (p. 35), and graphite (p. 118), which offer comparatively little *resistance* to the passage of the electric current; other materials, such as lime, sulphur, glass, shellac, and air, which offer great resistance to its passage, are termed *non-conductors* or *insulators*. There is, however, no sharp boundary line between the two classes; graphite, for example, is a bad conductor compared with copper, but a very good conductor compared with sulphur.

The pieces of metal used in a battery are termed the *electrodes* or *poles;* the electric current may be supposed to pass from one of the electrodes, which is called the *positive* (+) electrode, along the wire to the other, the *negative* (−) electrode (fig. 76), and then through the solution; the complete course taken by the electric current through the conducting materials is termed the *circuit*.

A current of electricity may be generated in other ways. By the combustion of coal or other fuels chemical energy may be first transformed into heat, and this form of energy may be used for driving a steam or gas engine; the latter may then be employed for driving a *dynamo*, a machine in which mechanical work is transformed into electrical energy; a dynamo may also be driven by machinery worked by water-power. By such means large supplies of electrical energy may be cheaply obtained.

Electrical energy may be again transformed into heat, light, chemical energy, &c. When an electric current is passed through a material which offers great resistance, and which is then said to be a bad conductor, electrical energy is transformed into heat. This occurs even if the material is a good conductor when its cross section is sufficiently small and the current is sufficiently powerful; the filament of carbon, tantalum, &c. in the incandescent electric lamp is thus raised to a white-heat by means of electrical energy.

Electrical energy may also be transformed into heat and light in another but similar manner. When an electric circuit is broken, say by cutting the wire through which the current is flowing, and the two ends of the wire are moved a short distance apart, a series of '*sparks*,' or a continuous luminous *arc*, passes between these two ends or *terminals*, provided that the current is sufficiently powerful. The arc light is produced in this manner between terminals which usually consist of graphite.

Electrical energy is very often used to bring about chemical change. For some purposes it is directly transformed into heat; that is to say, an electric current is simply used as a convenient means of producing a high temperature. Examples of this use have already been given. When electric sparks are passed between the platinum terminals of a eudiometer containing a mixture of oxygen and hydrogen, the gases combine (p. 189), just as they would do if a red-hot wire were placed in the mixture. Similarly, in the 'sparking' of hydrogen sulphide (p. 217), air (p. 247), and ammonia (p. 264), the effect produced is due to *heat* and not to any electrical action; a small proportion of the gas is momentarily raised to a very high temperature, and then, as it diffuses to another part of the tube, is suddenly cooled again.

The combination of nitrogen and oxygen, which is now brought about on a manufacturing scale by passing air through a large electric arc, first gives nitric oxide (p. 243). As this gas is decomposed at temperatures above 1200°, the air (which contains about 2 per cent. of this product) is rapidly cooled, and the nitric oxide then combines with more atmospheric oxygen, forming nitrogen tetroxide (p. 246). The tetroxide is led through an absorption tower, down which water is trickling, whereupon nitric acid is produced, together with nitric oxide,

$$3N_2O_4 + 2H_2O = 4HNO_3 + 2NO.$$

The nitric oxide thus formed combines with atmospheric oxygen, giving the tetroxide, which goes through the same absorption process as before.

The Electric Furnace.—When the current from a powerful dynamo (p. 298) is caused to form an arc between graphite terminals, enclosed in some fire-resisting (refractory) material which is also a poor conductor of heat—as, for example, quicklime—a temperature (3000°) far higher than any which can be reached by processes of combustion or other chemical changes may be attained. The apparatus used for this purpose is called the electric furnace, and one form of it is shown in fig. 77. It consists of two closely fitting slabs of quicklime, which are hollowed out, so that they enclose a small chamber, and also tubular spaces for the insertion of the graphite terminals. The material to be heated is placed in the chamber, below

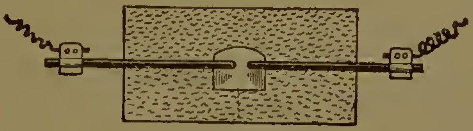

Fig. 77.

the arc, and the current is led to the graphite terminals by means of stout copper wires.

Instead of forming an arc between the two terminals, the latter may be placed much farther apart in a large chamber, and the space between and around them may be filled by the material which is to be heated, if the latter is a sufficiently bad conductor of electricity; on the current being passed, the material offers so much resistance that it becomes raised to a very high temperature, just as does the filament in an incandescent electric lamp.

The electric furnace is employed in the manufacture of phosphorus, aluminium, calcium carbide, carborundum, &c., and is principally worked in places where water-power is available.

Electrical energy is also employed in the form of the '*silent*' or *dark discharge* in bringing about chemical change. The apparatus often used for this purpose consists of two concentric glass tubes, the larger of which is covered on the outside, while the smaller is coated on the inside with tinfoil, as shown in fig. 78. When the two metal surfaces (a, a) are connected with the terminals of an induction coil, through which the current is passing, electrical discharge takes place quietly between the two glass surfaces, and a gas or vapour passing through the annular space between them may be chemically changed.

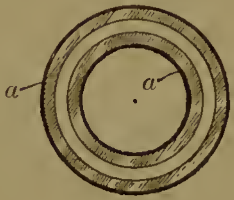

Fig. 78.

Electrolysis.—Aqueous solutions of different substances show a great difference in behaviour towards a current of electricity. If each of the electrodes of a suitable battery is connected by a conducting wire to a piece of platinum, and these two pieces of platinum (which may now themselves be regarded as the electrodes) are then immersed a short distance apart in a vessel of *distilled* water, no visible result is observed, and with the aid of a suitable electrical instrument (a galvanometer) it can be shown that the electric current does not pass. If, instead of water, the vessel contains an aqueous solution of sugar, again the current does not pass; but if the vessel contains an aqueous solution of some acid, basic hydroxide, or salt, not only does the current pass, but its passage is accompanied by the occurrence of chemical change.

Substances such as acids, basic hydroxides, and salts, aqueous solutions of which conduct electricity, are termed *electrolytes*, and the chemical change produced in such solutions by the current is termed *electrolysis* (Faraday). Substances such as cane-sugar, aqueous solutions of which do not conduct electricity, are termed *non-electrolytes.*

When a concentrated aqueous solution of hydrogen chloride is placed in a voltameter (fig. 43, p. 108) and an electric current of sufficient strength is passed, bubbles of chlorine rise from the positive electrode * (that which is connected with the positive pole of the battery) and bubbles of hydrogen rise from the negative electrode, but there is no evolution of gas except at the surface of the electrodes. The electrical energy is thus partly changed into chemical energy, the chemical energy of hydrogen chloride being far less than that of the system into which it is decomposed (p. 136). As pure water does not conduct electricity appreciably, whereas an aqueous solution of hydrogen chloride does so, giving hydrogen and chlorine, it may be concluded that it is the electrolyte which carries the electricity, and that in doing so its decomposition (electrolysis) is brought about.

Although in the electrolysis of hydrochloric acid equal volumes of hydrogen and of chlorine are set free, the volume of hydrogen which collects above the negative electrode is greater than that of the chlorine in the other limb of the voltameter. This is principally due, at first, to the *solubility* of chlorine being much greater than that of hydrogen, but even when the solution around and above the positive electrode is become saturated with chlorine, the volumes of the gases actually collected are not equal; this is because the pressure in the voltameter steadily rises, the solution becomes unsaturated (Henry's law, p. 164), and for any given increase in pressure the volume of the chlorine which dissolves is very much greater than that of the hydrogen.

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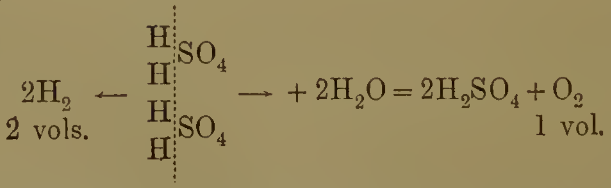
* The electrodes—that is to say, the surfaces from which the current enters and leaves the solution—are not made of platinum as are those (*c*, *c*, fig. 43, p. 108) in the voltameter previously described, because platinum is attacked by chlorine; they consist of graphite rods which pass through the india-rubber stoppers (*d*, *d*), and are connected with the poles of the battery by means of wires.

The electrolysis of a dilute aqueous solution of sulphuric acid (hydrogen sulphate) results in the liberation of oxygen at the positive electrode and hydrogen at the negative electrode (p. 108), the relative volumes of these gases being as 1 : 2. This fact seems to show that the water has been decomposed directly, and it can be proved experimentally that the sulphuric acid in the solution may be recovered unchanged, however long electrolysis is continued. Nevertheless it is concluded, for reasons which will be given later, that the hydrogen sulphate, like the hydrogen chloride in the preceding case, is really decomposed; that hydrogen is liberated at one (the negative) electrode, and the group of atoms, or radicle (SO_4), at the other. But this group or radicle immediately decomposes at the electrode, giving oxygen and sulphur trioxide, SO_3; the oxygen is liberated, while the sulphur trioxide combines with water to form sulphuric acid. According to this view, the final result may be expressed in the following manner,



$$\underset{2\text{ vols.}}{2H_2} \longleftarrow \begin{array}{l|l} H & SO_4 \\ H & \\ H & SO_4 \\ H & \end{array} \longrightarrow + 2H_2O = 2H_2SO_4 + \underset{1\text{ vol.}}{O_2}$$

and the oxygen may be regarded as a *secondary* and not as a direct product of electrolysis.

Aqueous solutions of other acids behave in a similar manner; on electrolysis hydrogen is liberated at the negative electrode, the other part of the acid molecule, or some secondary product, being set free at the positive electrode.

When an aqueous solution of sodium hydroxide is electrolysed, hydrogen is evolved at the negative and oxygen at the positive electrode, the relative volumes of these gases being as 2 : 1. In this case it is concluded that the sodium hydroxide molecules are decomposed, and that sodium is set free at the negative, the hydroxyl group or radicle (OH) at the positive, electrode. The sodium, however, immediately decomposes the water, giving hydrogen and sodium hydroxide, while the (OH) groups themselves decompose, giving oxygen and water. The final results may thus be accounted for.

When a solution of copper sulphate is submitted to electrolysis in the voltameter already described, or in the simpler form of apparatus shown in fig. 79, the negative electrode becomes coated with copper, and oxygen rises from the positive electrode. The salt is thus decomposed into copper, which is a primary product, and the (SO_4) group; but the latter then gives rise to oxygen as a secondary product, just as in the electrolysis of hydrogen sulphate.

The electrolysis of an aqueous solution of sodium chloride (using graphite electrodes, footnote, p. 301) results in the liberation of hydrogen at the negative and chlorine at the positive electrode. The chlorine is a primary product, but the hydrogen is a secondary product resulting from the action of the liberated sodium on the water,

$$\underset{1\text{ vol.}}{H_2} + 2NaOH = 2H_2O + \longleftarrow \begin{matrix} Na \vdots Cl \\ Na \vdots Cl \end{matrix} \longrightarrow \underset{1\text{ vol.}}{Cl_2}.$$

A solution of sodium sulphate gives on electrolysis hydrogen and oxygen, the relative volumes of the gases being as 2 : 1. If the solution is coloured with a little neutral litmus and electrolysed in the apparatus shown (fig. 79), it is seen that the liquid around the negative electrode becomes alkaline, whereas that around the positive electrode becomes acid to litmus. In this case the primary products of electrolysis are sodium and the (SO_4) group or radicle; the former acting on the water liberates hydrogen, while oxygen is liberated from the (SO_4) group as in the case of sulphuric acid,

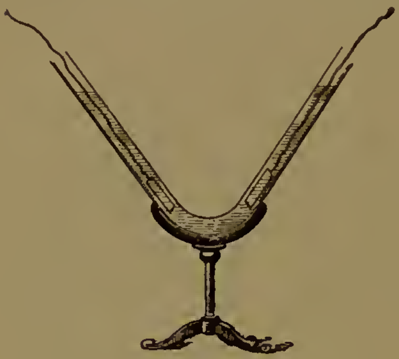
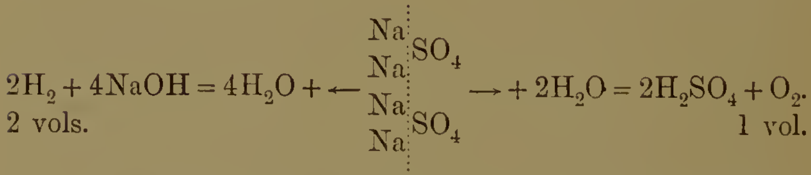


Fig. 79.



$$\underset{\text{2 vols.}}{2H_2} + 4NaOH = 4H_2O + \longleftarrow \begin{array}{r:l} \text{Na} & \\ & \text{SO}_4 \\ \text{Na} & \\ \text{Na} & \\ & \text{SO}_4 \\ \text{Na} & \end{array} \longrightarrow + 2H_2O = 2H_2SO_4 + \underset{\text{1 vol.}}{O_2}.$$

In consequence of these changes sodium hydroxide collects around the negative electrode and sulphuric acid around the positive electrode, but if the solutions in the two limbs of the voltameter are afterwards mixed the colour of the litmus shows that the solution, as a whole, is neutral.

From these examples of the electrolysis of acids, basic hydroxides, and salts, it would seem that the molecule of the electrolyte is decomposed into two parts. One of these parts is hydrogen or a metal, which is attracted to the negative electrode, and which, in consequence, is called *electro-positive.* The other part, which is attracted to the positive electrode, and which is called *electro-negative,* is either some element such as chlorine, or some group of elements such as (OH) or (SO_4). Some of these primary products are actually liberated and may be collected, but many of them either act on the water present or decompose, giving secondary products of electrolysis, namely, hydrogen in place of a metal, and oxygen (or some other substance) in place of the primary electro-negative element or group.

The behaviour of aqueous solutions of salts offers a simple means of finding which is the positive and which the negative pole of a battery; if the two wires from the battery are pressed a short distance apart on to a piece of blotting (filter) paper, moistened with a solution of sodium sulphate which has been coloured with neutral litmus, the colour changes to red around that wire which is connected with the positive pole of the battery, and to blue around the other wire.

Acids, basic hydroxides, and salts, which melt without decomposing, undergo electrolysis when in a fused condition. The primary products, which are stable under the conditions employed, are then obtained; thus the electrolysis of fused sodium chloride results in the liberation of chlorine and of sodium.

Many substances are now prepared commercially by electrolysis.

In all electrolyses the products are only liberated at the surfaces of the electrodes, although they may afterwards diffuse into the solution. It seems, in fact, that the electrolyte is decomposed into two parts, which *move* in opposite directions through the solution under the influence of the electric current. This may be accounted for by supposing that these parts carry electric charges, and that when they reach the electrodes they give up these charges, the carriers themselves being set free. These hypothetical charged particles which travel through the solution are called *ions;* that which is positively charged and which is attracted to the negative electrode or *cathode* is termed the *cation;* that which is negatively charged and which is attracted to the positive electrode or *anode* is termed the *anion.* It is only when these ions have given up their electric charges (at the electrodes) that the observed chemical changes occur.

It was proved experimentally by Faraday (in 1834) that the weight of any element which is liberated during electrolysis is directly proportional to the *quantity* of electricity which passes through the electrolyte; also, that *the weights of different elements which are liberated by the same quantity of electricity are directly proportional to their equivalents* **(Faraday's laws of electrolysis).**

When, for example, one and the same electric current is passed simultaneously through different vessels containing solutions of hydrogen sulphate, copper sulphate, and silver nitrate respectively, the weights of hydrogen, copper, and silver respectively liberated at the negative electrodes, and that of the oxygen liberated at one of the positive electrodes, are in the ratio 1 : 31·5 : 107·1 : 7·94, which is the same as that of their equivalents (p. 174).

It is thus possible to determine the equivalent of an element (most easily in the case of certain metals) by passing the same current simultaneously through an aqueous solution of hydrogen sulphate and through a solution of some salt of the element. The volume of hydrogen liberated from the hydrogen sulphate, and the weight of the metal deposited from the salt in the same time, are determined, and the equivalent of the metal may then be calculated.

Example.—40 c.c. of hydrogen at N.T.P. are liberated and 0·1134 g. of copper is deposited in a given time. The *weight* of the hydrogen is 0·0036 g. The equivalent of copper, therefore, is $\frac{1 \times 0{\cdot}1134}{0{\cdot}0036} = 31{\cdot}5$.

In the case of elements which have two or more equivalents, the weight of the element liberated by a fixed quantity of electricity depends on the compound of that element which is electrolysed, but the equivalents determined electrolytically (sometimes called electro-chemical equivalents) and chemically, with any given compound, are the same.

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[Where more than one reference is given, the one in heavy type refers to the more important or systematic description of the subject.]

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